IDENTIFICATION AND INTERPRETATION OF MINERALOGICAL INFILTRATION OCCURRING IN A CHROME REFRACTORY COLLECTED IN THE SUDBURY, ONTARIO REGION

A Thesis

Presented in Partial Fulfillment of the
Requirements for the Degree Bachelor of Science

by

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1985

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ABSTRACT

The purpose of this paper is to explain the mineralogical changes that have occurred in a brick taken from a Sudbury copper smelter. A distinct color change is observable across a slab cut from the brick. The scanning electron microscope and computer x-ray analysis program explain the color changes. The x-ray images obtained indicate the brick is composed of magnesia and chrome spinel with very poor crystal bonding. It is this poor bonding that allows material to infiltrate the brick. It was found that copper was the major infiltrated element; however, trace amounts of sulfur, iron, and nickel also were observed. It appears that these elements derived from the processed ore do affect the mineralogy. The color change is the result of new minerals infiltrating the brick matrix. Native copper and cuprite have been clearly identified and there is a strong possibility that additional copper, iron, and nickel minerals have infiltrated to a lesser degree. Many figures illustrate, identify and explain the color changes caused by mineral infiltration.

ACKNOWLEDGEMENTS

I wish to thank the Friends of Orton Hall for their generous gift. Their grant allowed me to obtain data on the scanning electron microscope that would have been otherwise unobtainable. I would like to thank Dr. G. D. McKenzie for providing the sample used in this report. I also wish to thank Dr. D. E. Pride for his suggestions and help given throughout this project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES

TABLES

INTRODUCTION

A variety of equipment was used to gather data for this thesis. This topic is somewhat unusual and it was unclear as to what data might be the most useful. To explain the mineralogy of the brick a series of thin sections were made, realizing this brick is mainly opaque a similiar series of polished sections were also prepared. To help identify minerals present in the sections a series of x-ray diffraction patterns were taken. These three datum confirmed one another yet didn't give enough information. It was then decided to place a series of samples in the scanning electron microscope. The SEM filled the void of information and actually gave the best quantitative and qualitative results. Computer programs used inconjuction with the SEM provided information on brick composition and mineral infiltration. The SEM produced clear micrographs showing crystal bonding and structure. A program called MSCAN was used for acquisition and display of both x-ray and video images. Photographs showing composite x-ray and video image brilliantly illustrate composition and infiltration of new minerals. Acquired x-ray spectra used in a program called SSQ provided a standardless semi-quantitative analysis of the brick. Overall the SEM provided quantitative results and quality illustrations. Figure 1. a cross-section of the Sudbury brick illustrates the color changes, as they appear on a freshly cut surface. These color changes are explained by information gathered using the above mentioned instruments and equipment.

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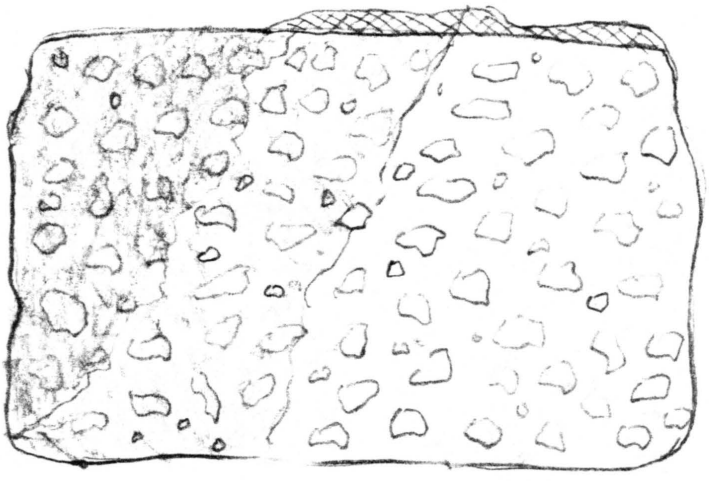

Figure 1.
Cross section of Sudbury brick illustrating color chages.

GEOLOGIC SETTING

The geology of the Sudbury region is presented in order to explain the basic premise which is; To identify and interpret and mineralogical changes that have occured as a result of mineral infiltration. Minerals have infiltrated a refractory (brick) dirived from a copper smelter. These minerals originated from copper ore mined in the Sudbury region. There are many types of ore mined at Sudbury. The bulk of the disseminated ore is associated with the quartz diorite phase of the norite (Hawley 1962). Figure 2. a geological sketch map of the Sudbury area shows the location of ore processed through the smelters (Thomson 1969). Other ores processed include massive ores composed almost entirely of sulphides with variable amounts of magnetite. Breccia ores are everywhere and quantitatively very important. Some vien and stringer ores are present but most nickel-copper ores are dirived from the massive type ores (Hawley 1962). Figure 2. also lists rock composition of formations which when processed as gangue; account for some minerals which may have infiltrated the refractories.

A more extensive list of minerals found in the Sudbury ores is listed in Table 1.(Hawley 1962). Any of these minerals may have infiltrated the refractory and effect the mineralogy within the refractory. The most abundant minerals present in the ores will most likely have the greatest effect on the infiltration of the refractory. The four most abundant minerals are pyrrhotite, pentlandite, chalcopyrite and cubanite, which constitute the major part of the many Sudbury ore deposits and are chiefly responsible for its economic exploitation (Hawley). The four elements associated with these minerals are Cu, Fe, Ni, and S, these are the elements that will be searched for in the refractory samples. In order to observe changes caused by the influx of these elements the smelting industry and the refractory composition are discussed.

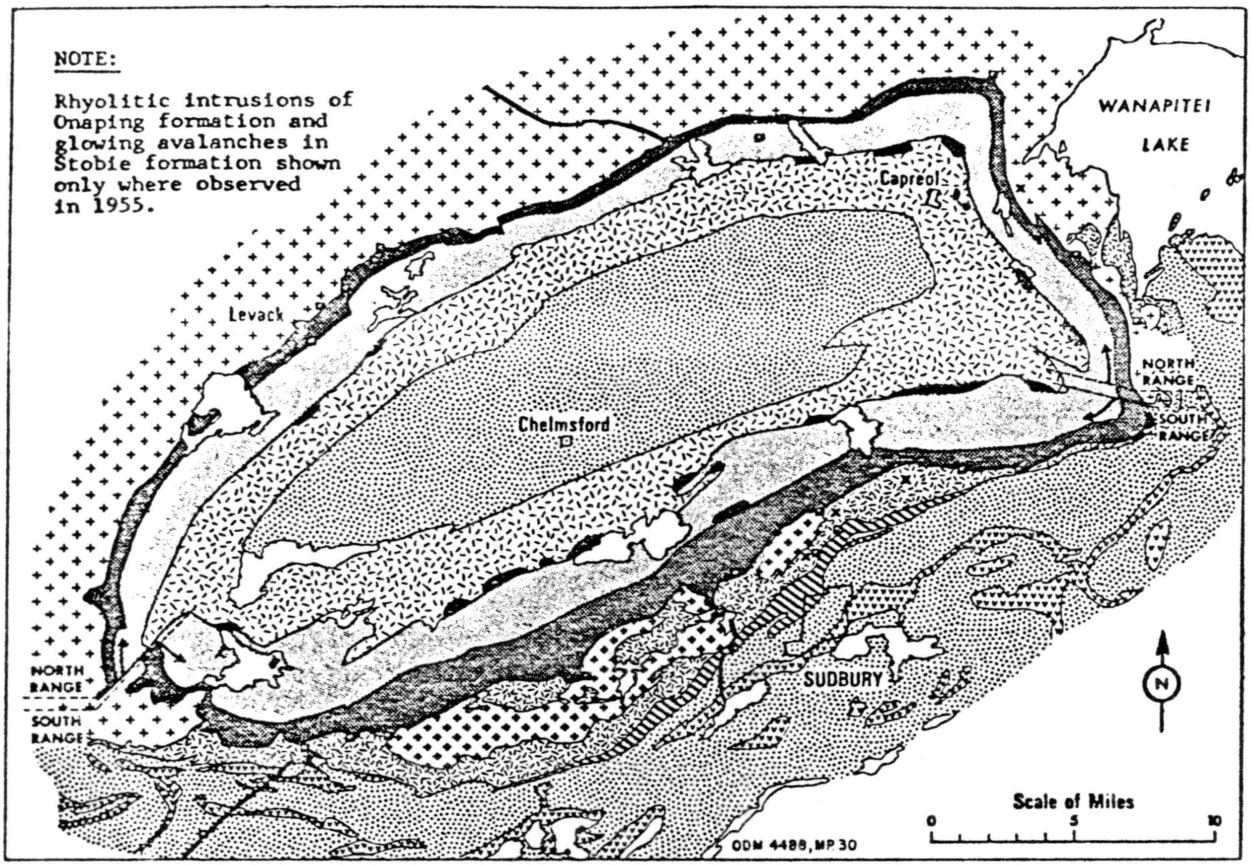

Figure 2 — Geological sketch map of the Sudbury area (modified after Fig. 5, O.D.M., Vol. 65, 1956, pt.3, p.67).

LEGEND

PRECAMBRIAN

INTRUSIVE ROCKS

- Post-norite granitic intrusions
- Granophyre
- Norite
- Sudbury gabbro
- Pre-norite granitic intrusions
- Copper Cliff rhyolite

ONWATIN-CHELMSFORD FORMATION

- Argillite, greywacke, arkose (located inside of norite-granophyre)

McKIM-MISSISSAGI FORMATION

- Greywacke, quartzite, conglomerate (located outside of norite-granophyre)

ONAPING FORMATION

- Rhyolitic intrusions (dike-feeders)
- Glowing avalanche deposits: coarse tuff-breccia and lapilli tuff (located inside of norite-granophyre)

STOBIE FORMATION

- Lavas, sediments, rhyolitic intrusions, glowing avalanche deposits (Glowing avalanche deposits marked x, located outside of norite-granophyre)

- Mine (sulphides)

TABLE 1. Minerals in the Sudbury Ores

Type	Mineral		Occurence
METALLIC MINERALS			
Native Metals	Gold		rare
and Semimetals	Silver		"
	Bismuth		"
Tellurides	Tetradymite	Bi_2TeS	"
Sulphides	Hessite	Ag_2Te	"
Arsenides	Chalcocite	Cu_2S	"
Bismuthides	Maucherite	$Ni_{11}As_8$	"
	Heazlewoodite	Ni_3S_2	"
	Bornite	Cu_5FeS_4	"
	Galena	PbS	minor
	Sphalerite	ZnS	minor
	Chalcopyrite	$CuFeS_2$	common
	Stannite	Cu_2FeSnS_4	rare
	Pyrrhotite	$Fe_{1-x}S$	common
	Valleriite	$Cu_2Fe_4S_7$	rare
	Niccolite	$NiAs$	minor
	Millerite	NiS	rare-secondary
	Pentlandite	$(Fe,Ni)_9S_8$	common
	Cubanite	$CuFe_2S_3$	minor
	Violarite	Ni_2FeS_4	minor-secondary
	Bismuthinite	Bi_2S_3	rare
	Pyrite	FeS_2	minor to common
	Pyrite(nickeloan)	$(Fe,Ni)S_2$	rare
	Molybdenite	MoS_2	reported
	Sperrylite	$PtAs_2$	rare
	Michenerite	$PdBi_2$	rare
	Froodite	$PdBi_2$	rare
	Gersdorffite	$NiAsS$	minor
	Marcasite	FeS_2	minor-secondary
	Cobaltoan arsenopyrite	$(Fe,Co)AsS$	reported
	Parkerite	$Ni_3Bi_2S_2$	rare
	Smaltite	$(Co,Ni)As_{3-x}$	reported
Sulphosalts	Tetrahedrite	$(Cu,Fe)_{12}Sb_5S_{13}$	reported
	Schapbachite	$AgBiS_2$	rare
Oxides	Magnetite-Ilmenite	$Fe_3O_4 - FeTiO_3$	common
	Hematite	Fe_2O_3	rare
	Cassiterite	SnO_2	reported
Hydrous Oxides	Limonite(Goethite)	$Fe_2O_3*nH_2O$	secondary
Sulphates	Chalcanthite	$CuSO_4 * 5 H_2O$	secondary
	Melanterite	$FeSO4 * 7 H_2O$	"
	Morenosite	$NiSO_4 * 7 H_2O$	"

NON-METALLIC MINERALS

Fluorite, Calcite, Solomite, Siderite, Quartz, Albite, Labradorite, Hypersthene

GANGUE MINERALS

Hornblende, Actinolite, Hastingsite, Sericite, Biotite, Clinochlore and peninnite, Almandine, Zircon, Titanite, Prehnite

After J.E. Hawley 1962, p 41-42.

HISTORY OF THE SUDBURY REGION

The history of the smelting industry in the Sudbury, Ontario region is presented in order to give the background information of this refractory. The Canadian Copper Company was the first company which seriously undertook the business of mining in this area. In May of 1886, work started at the Copper Cliff mine where ore was obtained from the surface openings of the original Copper Cliff mine (Barlow 1904). The first smelters were built in 1886 and as Barlow states the first blast furnace was blown in on December 24,1888. Earlier attempts to mine this area had failed. But as far back as 1770, the existence of workable deposits of copper in the region had long been known. Many of these early companies failed because of the remoteness from civilization and any market for the ore. However after a cutting made by the Canadian Pacific Railway in 1884, the extent of ore made this deposit one of the most promising yet seen in Canada (Barlow 1904). The first smelters and blast furnaces were built in the 1880's many have since been built and abandoned. Because of this it is impossible to tell the date of construction of the smelter from which this refractory originated. However it was collected from one of the abandoned smelters. In order to determine mineralogical changes its age is not as important as is the initial composition.

COMPOSITION OF REFRACTORY

The initial composition of the refractory was unknown. Thus the first part of this project was to determine initial composition thereby allowing easier interpretation of mineralogical changes. Large peaks of Magnesium (Mg) and Chrmiun (Cr) were discovered from x-ray data. These peaks were found not only in x-ray diffraction patterns but also in every x-ray spectrum acquired using the scanning electron microscope. Chromium is not listed in any of the Sudbury ores contained in Table 1. Magnesium although present in small quantities in nonmetalic minerals in Table 1., was considered too small in concentration to have any effect on infiltration. Thus chromium and magnesium appeared to compose the majority of this copper-smelter refractory.

This assumption is easily backed referencing A.V. Petty. Chromite ore in combination with various quantity of magnesia, is employed in the manufacture of basic refractories (brick). Refractories of this type are used as linings in copper-smelting furnaces (Petty 1982). The addition of MgO (magnesia) with chromite ore will cause the formation of forsterite on firing (Norton 1968). The mineral composition is very important in chrome and magnesia refractories because of the effect that mineral composition has on the bonding of the material and its purification (Coxey 1950). Assuming fairly pure concentrations of magnesia and chromite ore, the initial composition of the refractory is chromite, magnesia and forsterite. These three minerals from the crystal to crystal boundaries present in the refractory. Further evidense is given by Petty who states; magnesia-chromite (mag-chrome) refractories are engineered so that the relatively impure chromite grains react at their surfaces with relatively clean magnesia to form grain boundary spinels (Petty 1982).

What is the composition of a relatively impure chromite grain. An analysis of chromite ores is given in Table 2. (Norton 1968). The chromite ore in this table shows a large amount of impurities. These impurities include magnesia,

iron oxides and aluminum oxide which add up to more than 50% of the ore composition. This composition tends to indicate that the initial composition of the brick is not chromite and magnesia but chrome spinel and periclase (magnesia). This is consistant with the report by A.V.Petty and E. Martin 1981. They found chrome spinel $(Fe^{+2},Mg^{+2})O * (Al^{+3},Cr^{+3},Fe^{+3})_2O_3$, periclase (MgO), and minor amounts of forsterite (Mg_2SiO_4) in all their samples. Based on SEM analysis and x-ray diffraction data, polished section data, and based on visual observations found in my photomicrographs and compared to those found in a paper by McLendon et al.(1979), the initial composition of the Sudbury brick appears to be chrome spinel, periclase, and forsterite.

TABLE 2 Analysis of Chromite Ores, Refactory Grade

Constituent	Philippine Lump	Philippine Concentrate	Transvaal Lump	Transvaal Concentrate
SiO_2.....	5.1	2.8	2.8	0.8
Al_2O_3.....	27.9	29.5	15.0	17.4
FeO.....	13.0	13.9	24.1	24.6
CaO.....	0.5	0.4	0.3	0.2
Cr_2O_3.....	33.2	34.4	46.3	47.3
MgO.....	18.7	17.3	10.6	9.7
Ignition loss	1.1	1.0	0.3	0.1

after F. H. Norton 1968, p.84.

ENERGY - DISPERSIVE X-RAY ANALYSIS

Energy-dispersive analysis of x-rays showed only Mg, Al, Si, Cr, Fe, and Ca as the major elemental constituents of the samples (Petty 1982). This coincides with the analysis of x-rays produces by the Sudbury brick, except that those x-rays showed a substantal amount of copper as well. This is my first indication that copper has infiltrated this brick. However traces of S, K, and Ni were also observed in the brick. Appendix I of this report lists in order the x-ray spectra collected on samples 1,2,3,5 and 7. Figure 3. illustrates where the samples were collected from the brick. Appendix II describes preparation of the Sudbury brick samples. In order to give more meaningful results of the spectra in appendix I, a semi-quantitative analysis was run on those spectra.

SEMI-QUANTITATIVE ANALYSIS

A table has been prepared with the results from the semi-quantitative analysis program. Table 3 lists the relative weight percent in excitation volume for a number of elements in each sample. Some samples have more than one spectrum, thus are sub-lettered after the sample number. In order to run this program a take-off angle (TA) had to be figured. This was accomplished by taking into account the working distance (WD) and tilt of the specimen. This data was acquired during operation of the SEM and is recorded in Table 3. The formula used to figure out this take-off angle (TA) is :

$$TA = \arctan (50 / 9.1 - WD) + 0.707 (tilt) - 90^{\circ}$$

(after D.W. Foreman 1985)[1]

What the table shows is a relative weight of many elements which can be used to check against known mineral weight percentages. A comparison of Table 2. to Table 3. shows that the composition of the Sudbury brick is not chromite but more like chrome spinel.

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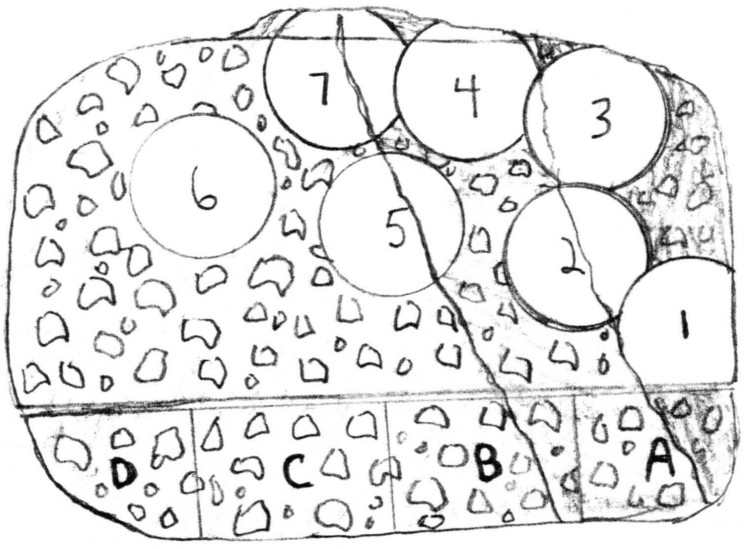

Figure 3.
Cross section of Sudbury brick indicating locations of brick samples used in SEM analysis and samples used in x-ray diffraction.

TABLE 3 Semi-Quantitative Analysis

	SAMPLE #									
	1-A	1-B	1-C	2-A	3-A	3-B	5-A	5-B	7-A	7-B
Working distance	11.5	6.0	10.0	8.5	8.0	9.1	8.5	10.0	6.5	8.5
Tilt	40	40	40	40	40	40	40	40	40	40
Take-off angle	30.7	24.7	29.0	27.6	27.0	28.0	27.6	29.0	25.3	27.6
RELATIVE WEIGHT PERCENT Mg%	49.5	43.9	14.3	33.2	43.6	34.7	45.3	33.8	23.3	41.8
Al%	5.5	8.6	4.2	14.6	14.9	16.7	11.9	9.8	21.3	9.4
Si%	4.9	6.5	0.9	2.0	9.3	5.2	8.0	3.8	2.8	5.0
S%	0.5	-	0.6	-	0.9	0.7	1.0	-	-	-
K%	-	-	0.1	-	0.3	0.2	0.3	-	-	-
Ca%	0.4	0.6	0.3	0.4	2.2	1.7	2.5	1.3	1.0	1.7
Cr%	1.6	2.7	1.5	10.0	14.4	23.9	12.6	5.6	18.8	5.2
Fe%	4.7	5.3	2.1	7.7	10.3	11.6	10.8	6.1	8.1	6.4
Ni%	-	-	-	0.3	-	-	-	-	-	-
Cu%	33.2	32.4	75.9	31.7	4.2	5.3	7.6	39.8	24.7	30.4

SEM MICROGRAPHS & X-RAY AND VIDEO IMAGES

A very effective way to illustrate crystal identification and determination is to use both SEM micrographs and mapping data. Mapping data includes both elemental x-ray distribution images and video images as well as composite images made from both. Figure 4. a micrograph of sample #1-B clearly shows three different crystals. When used inconjunction with figure 5. the three different crystals become clear. Figure 5. shows a x-ray image of four elements on left side. On the right side is a video composite image showing the distribution of both magnesium (red) and copper (blue), over-lap of the elements produce the lighter violet color. What these two figures show is that chrome spinel crystals are present in the upper left-hand corner. Periclase is the remaining crystals with a copper network streching around both the periclase and spinel crystals.

Perhaps another set of figures will explain the determination of the crystal composition. Figure 6. a micrograph of sample #2-A shows distinct crystals of periclase (left side) and chrome spinel (right side). A x-ray image and composite video of figure 7. show the location of three major elements. The composite video shows distinct crystal forms by color coding periclase (red), copper (blue) and chrome spinel (yellow-green). The x-ray map of Fe shows a high concentration of this element in the spinel crystal, further proof that the crystal is chrome spinel and not chromite.

In order to give a series of x-ray maps that include Mg, Al, Si, Ca, Cr, Fe, and Cu, figures 8. and 9. are included. Figure 8. is a SEM micrograph of the area in which the x-ray maps were acquired. Figure 9. shows the distribution of seven elements giving further proof as to the composition of the Sudbury brick. Figure 9. also shows some evidense for the formation of forsterite as it shows the distribution of Mg (red), Si (blue), and Ca (yellow) which closely resembles the map of Si.

Micrographs observed in a paper by McLendon et al.(1979), show similiar distribution of Mg, Ca, and Si around crystals supporting their analysis of forsterite in their samples. Although the evidence for forsterite is weak it is probable that some was produced upon firing of this refractory.

Other evidence for the identification of crystals is given in figures 10. and 11. Figure 10. shows a large crystal of chrome spinel in the center of the micrograph. An x-ray analysis of the area is illustrated in figure 11. This high chromium content together with other observations such as x-ray maps identifies this grain as chrome spinel.

Figure 4.
SEM micrograph of sample #1-B showing composition of crystals when used with x-ray images provided below.

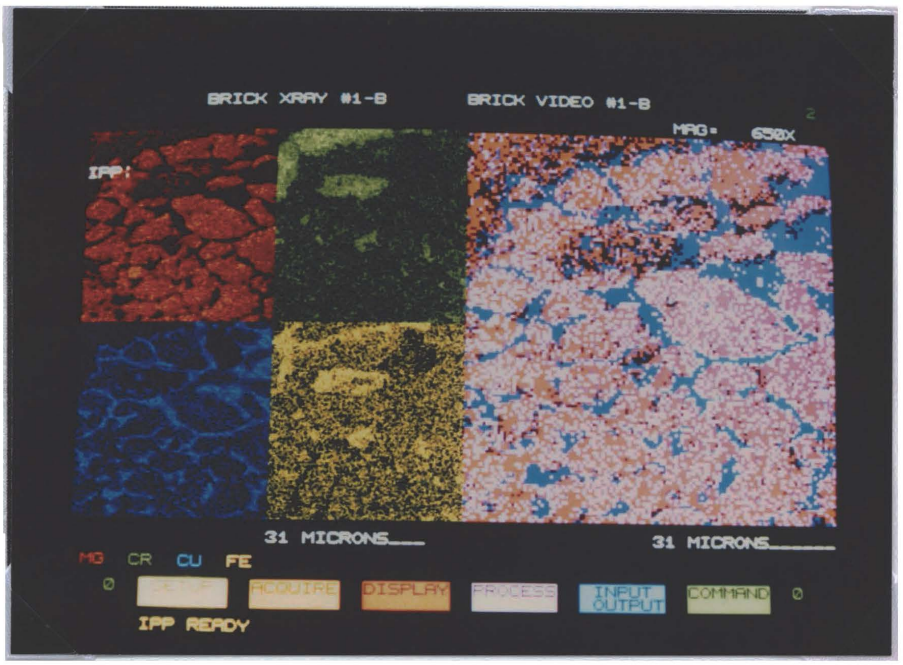

Figure 5.
Photograph of x-ray images and composite video image showing distribution of Mg (red) and Cu (blue) in sample #1-B.

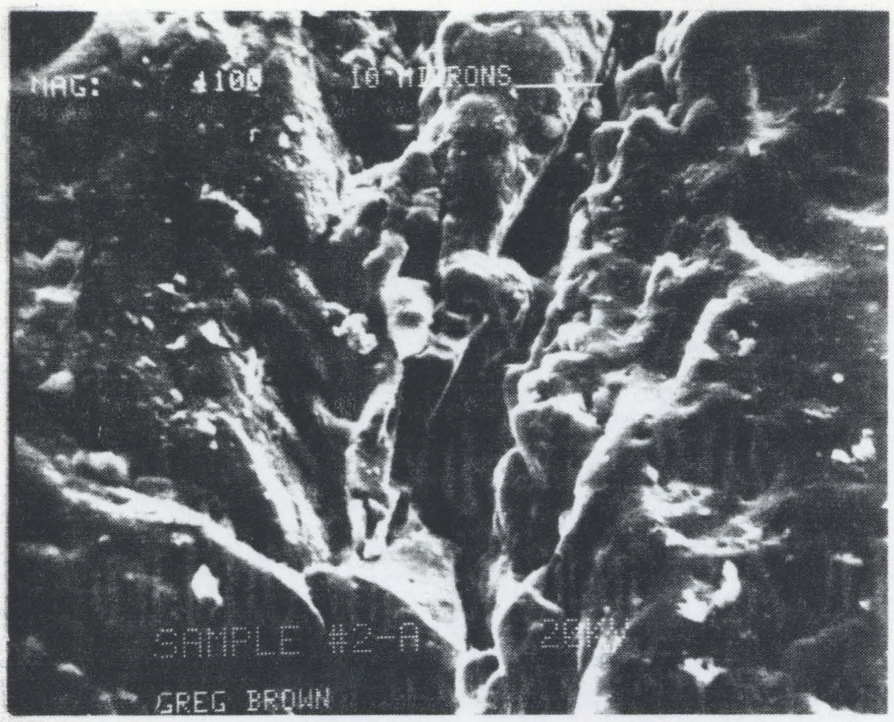

Figure 6.
SEM micrograph of sample #2-A showing composition of brick. Use with x-ray images provided below.

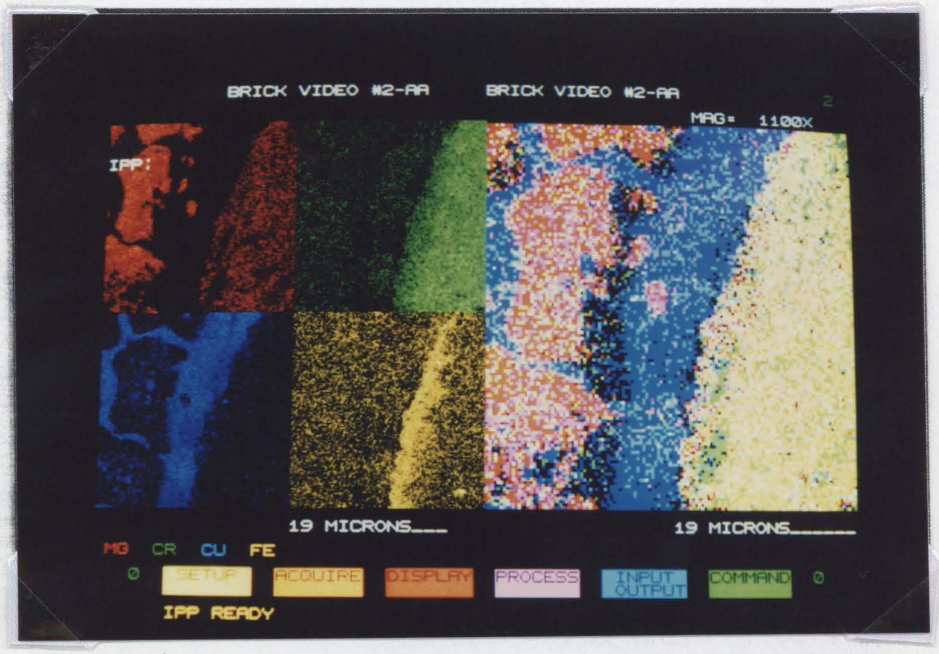

Figure 7.
Photograph of x-ray images and composite video image showing distribution of Mg (red), Cr (green), and Cu (blue) in sample #2-A.

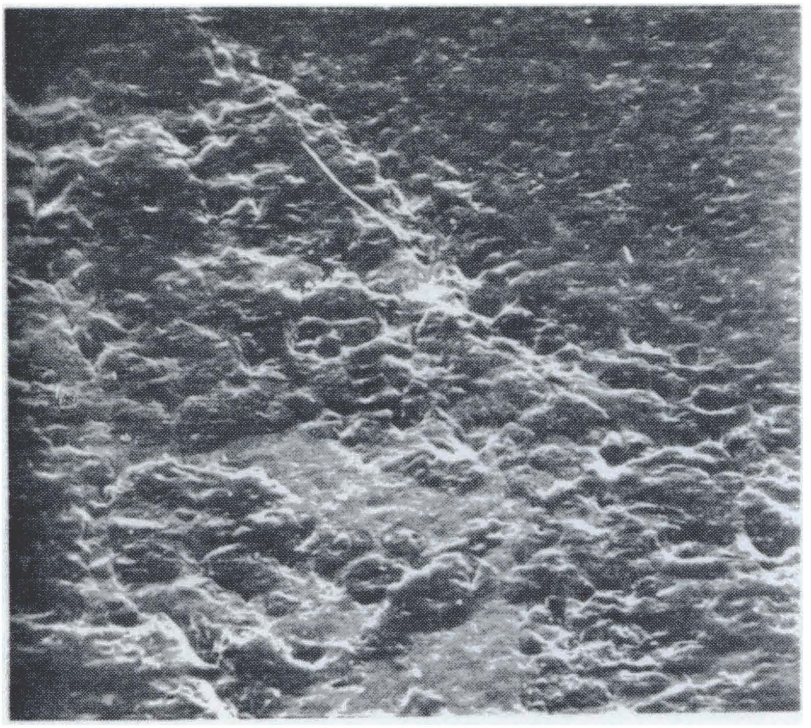

Figure 8.
SEM micrograph of sample #7-A, use with x-ray images provided below. Width of photo is 440 microns.
Mag. 220x.

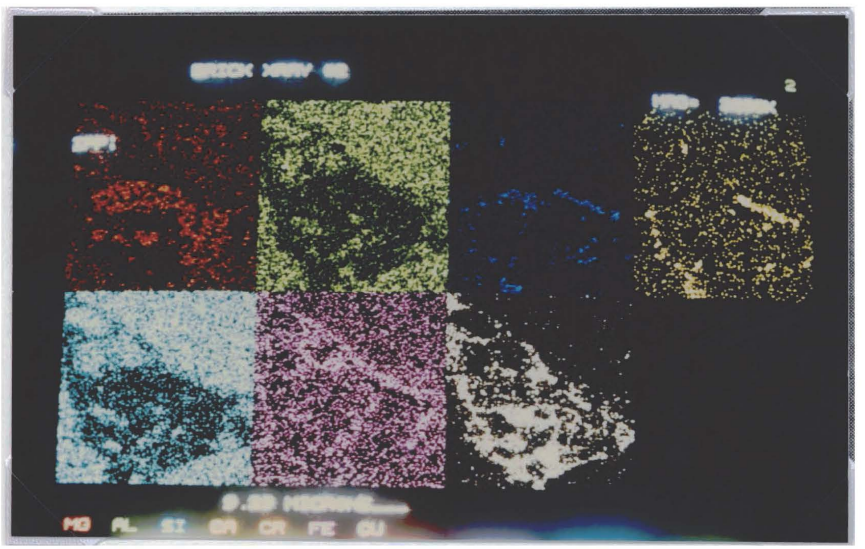

Figure 9.
Photograph of x-ray images of sample #7-A showing distribution of Mg, A1, Si, Ca, Cr, Fe, and Cu.
Note location of Si and Mg, possible evidence for the presence of forsterite.

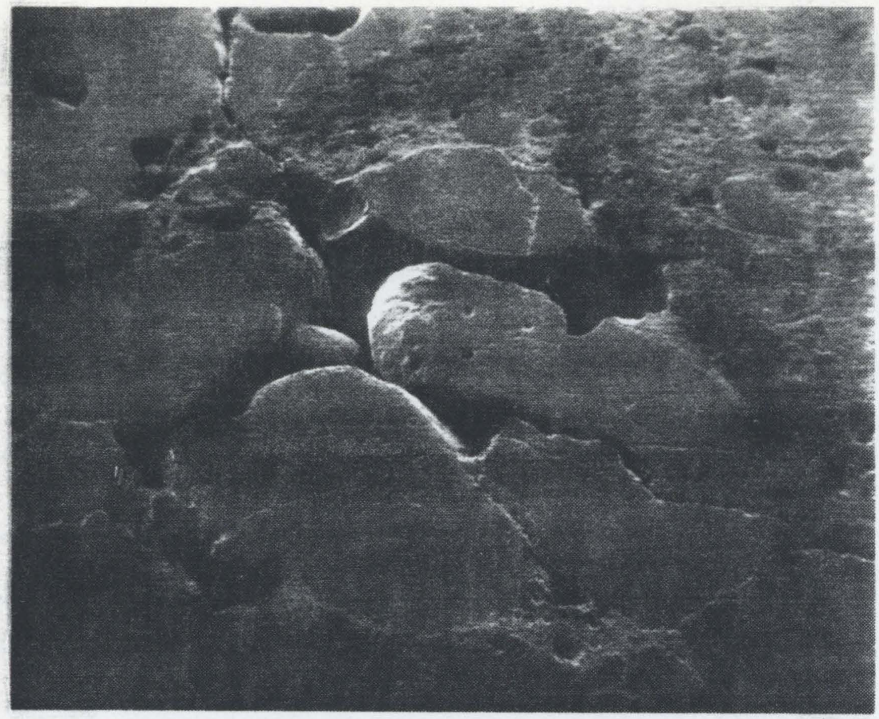

Figure 10.
SEM micrograph of large grain in sample #1. Photo width is 5mm. Mag. 20x.

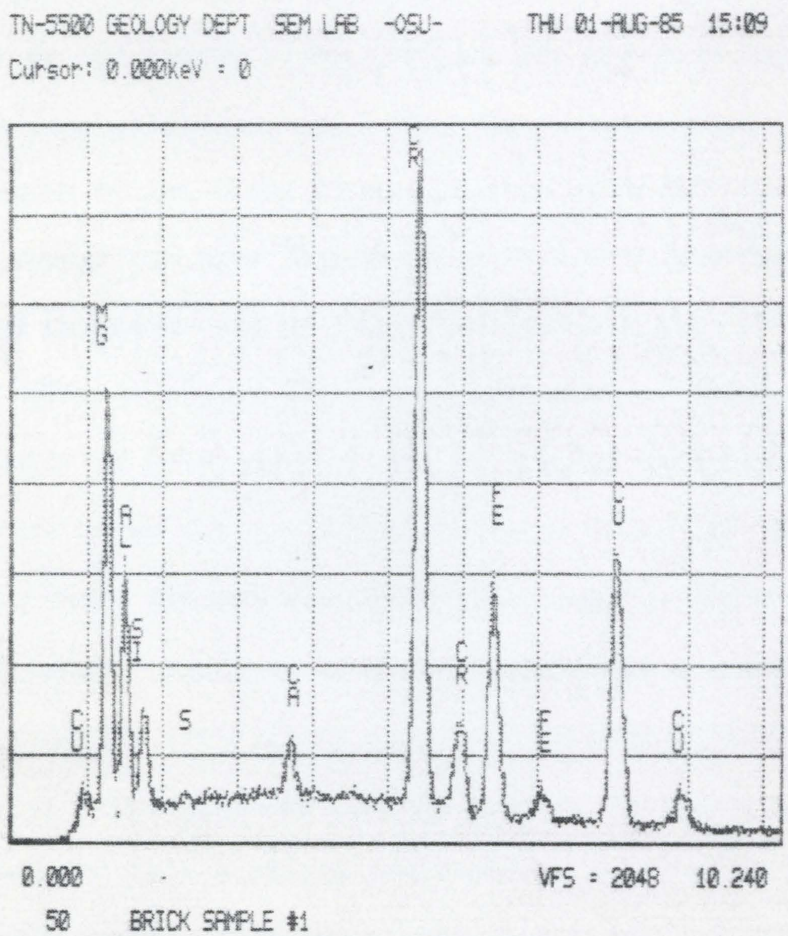

Figure 11.
X-ray analysis spectrum of sample #1 identifying large grain in figure 21.

What the crystals are has been discussed but how and what has infiltrated them has not. Referring back to figure 1. which illustrates color changes in the brick, how might some substance infiltrate to the extent that it has in what appears to be a solid brick. It appears solid but upon closer inspection it contains many voids between crystals. McLendon et al.(1979) states it is common for voids to occure at crystal boundaries. However voids between crystals in figure 12. are much more extensive than any observed in the paper by McLendon et al. Even at higher magnification voids are present between the smallest of grains as seen in figure 13. With such space between crystals present throughout the brick it is safe to assume that this is the route taken by infiltrating material (elements and minerals).

Figures 14. and 15. show exactly how for example copper infiltrated the matrix. Figure 14. shows four x-ray images that allow identification of crystals present in the nearby video. Figure 15. the same sample shows the x-ray images and composite x-ray map. Here Mg is designated by the color red and Cu is designated by the color blue. Overlap is violet colored. This figure illustrates how copper may have flowed threw this pore and filled in some of depressions. The composite map of figure 15. shows a sort of topographic map of the sample. Refer to figure 13. for a clear view of this area.

Another example of void space common in crystal boundaries is illustrated in figure 16. Here large vallies funnel material threw the brick matrix. Voids as large as these are not common in chrome-mag refractories as was observed in a paper by McLendon. Voids as large as these could account for the great extent that material has infiltrated into this Sudbury refractory.

Based on x-ray mapping, video images, spectra analysis, x-ray diffraction patterns, polished and thin sections and based on information found in a paper by Petty and Martin (1981), it appears that copper has infiltrated this brick. As descibed by Petty and Martin (1981), metallic copper was visible in the

refractory. Apparently liquid copper penetrated cracks and voids that developed in the brick during the furnace campaign and subsequently solidified into large pieces of metallic copper after furnace shutdown. At higher magnification figure 17. shows one bleb of copper that ... grouped together in figure 16. As additional proof that figure 17. is copper, an x-ray analysis is presented as figure 18. This shows minor element concentrations but is overwhemingly copper as shown by the copper peaks.

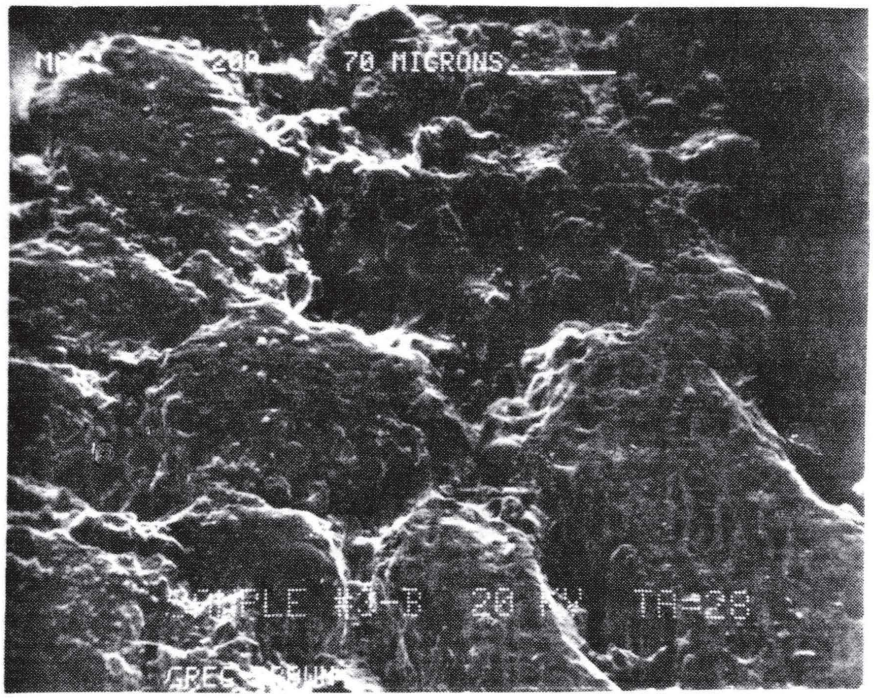

Figure 12.
SEM micrograph of sample #3-B showing crystal to crystal bonding. Notice large amount of void space.

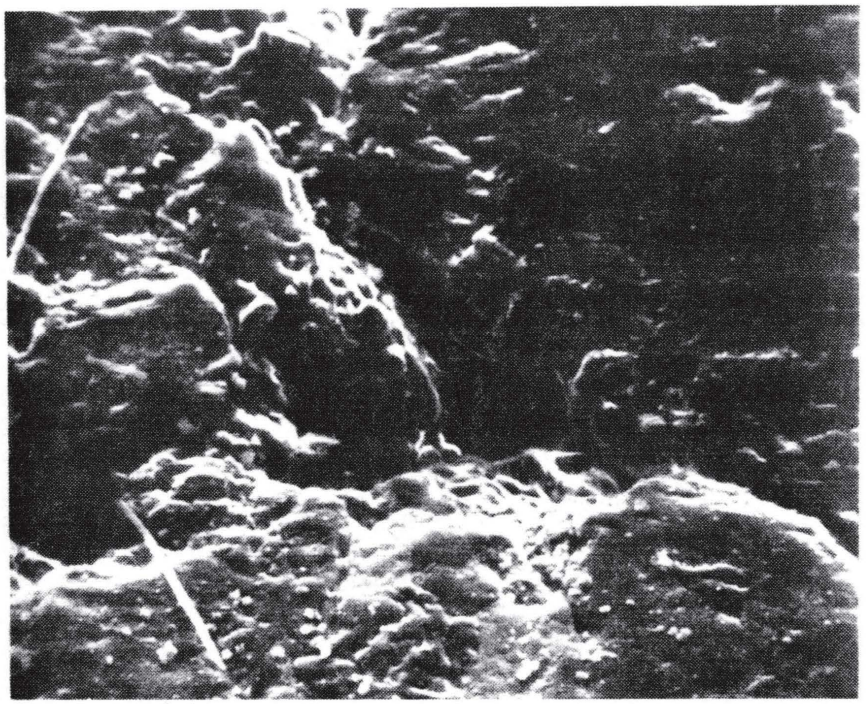

Figure 13.
SEM micrograph of sample #7-B showing pore space between crystals. Width of photo is 125 microns
Mag. 550x

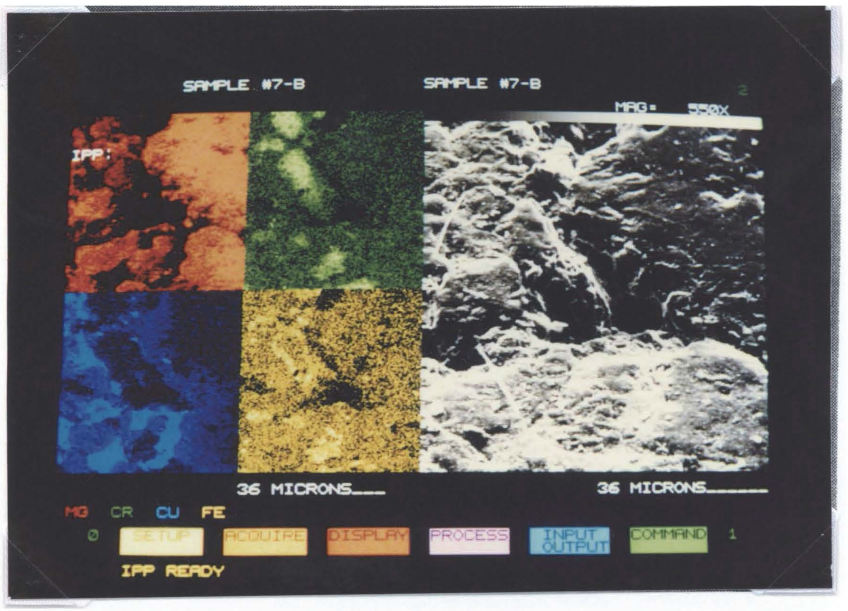

Figure 14.
Photograph of video and elemental x-ray distribution images of sample #7-B.

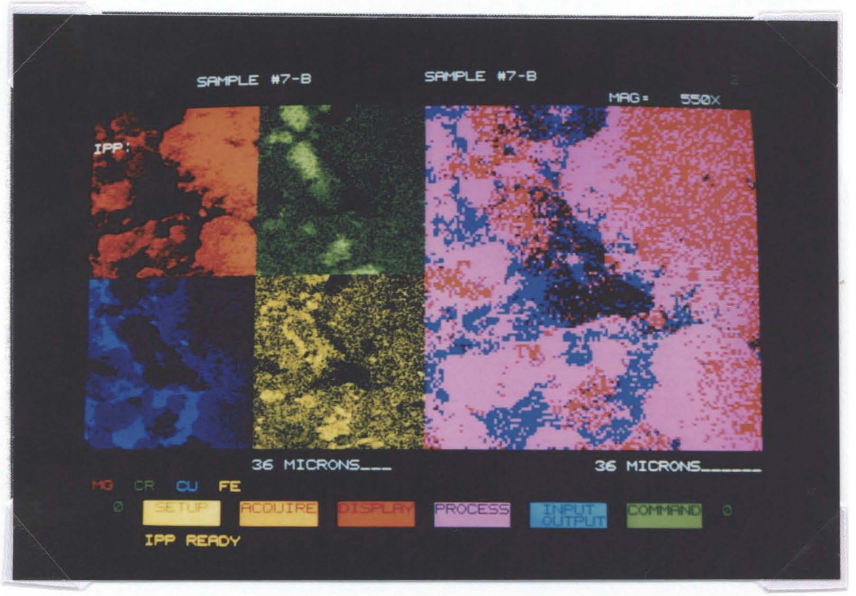

Figure 15.
Photograph of x-ray images and composite x-ray image showing distribution of Mg (red) and Cu (blue) in sample #7-B. Refer to figure 13. for a micrograph of this area.

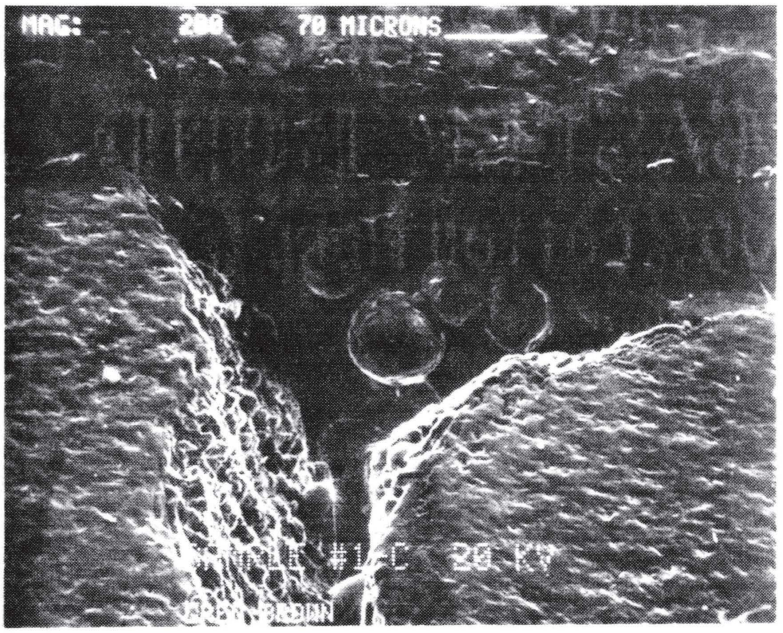

Figure 16.
SEM micrograph of sample #1-C showing gaps between crystal bonds with in-filling of copper.

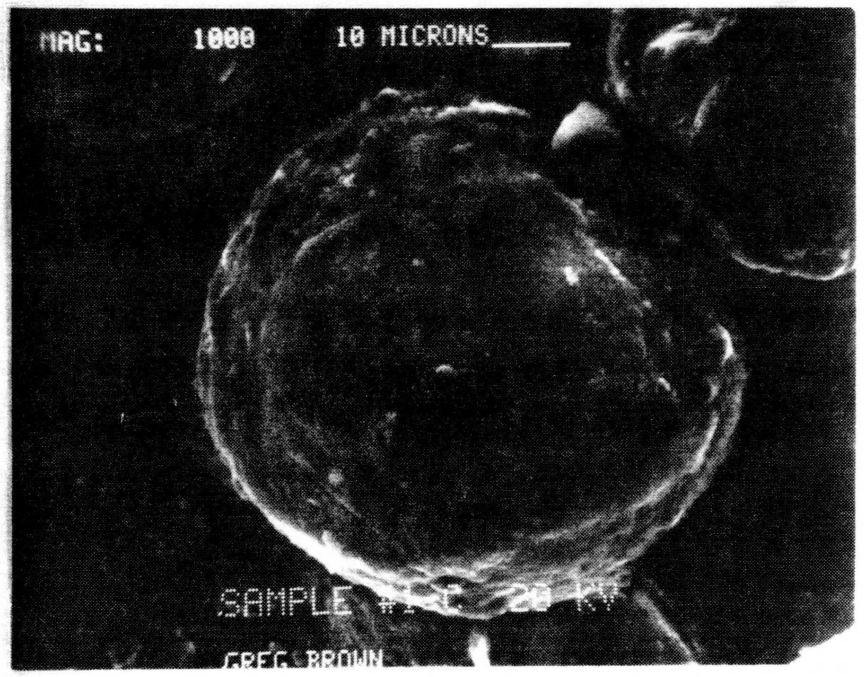

Figure 17.
SEM micrograph of sample #1-C showing shape of infiltrated copper.

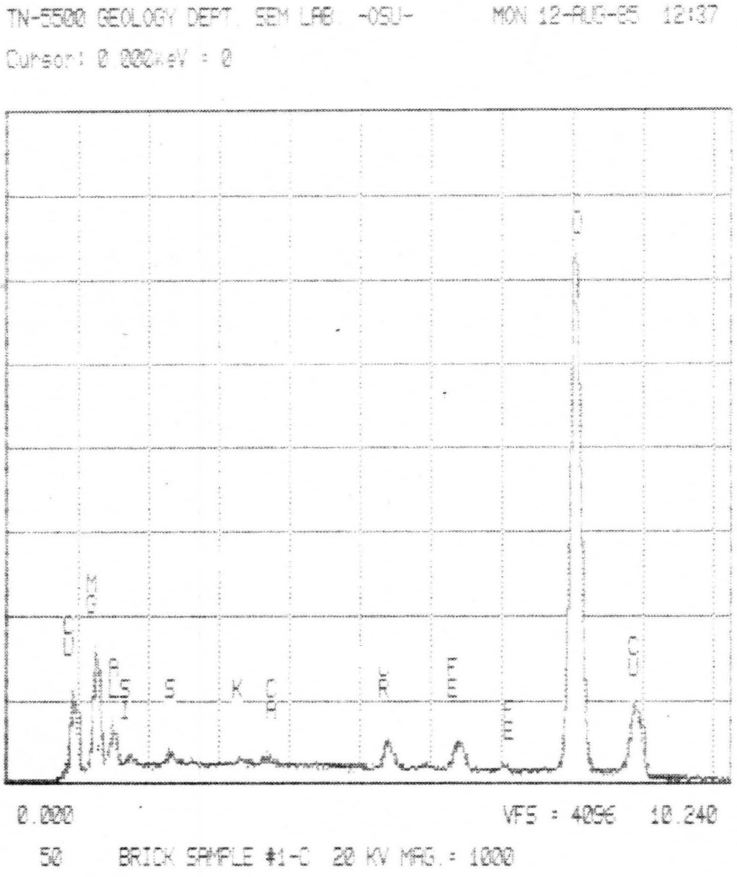

Figure 18.
X-ray analysis spectrum of sample #1-C incompassing area shown in figure 17.

What other elements maight have infiltrated. Previously mentioned was evidence for trace amounts of S, K, and Ni. Magnesium and iron were also present in large amounts. Any of these elements could have combined together or with copper to form different minerals yet there is no evidence for this. Many of the trace elements were not found in significant quantities to form minerals. None of the trace elements were found far into the brick. Yet there is a large area of discoloration that extends far into the brick. From all the evidence gather from SEM analysis it appears that copper is the only element to infiltrate the whole brick.

Further evidence of copper infiltration is shown in figures 19. and 20. These figures show copper filling voids such as a mud slide might fill a river valley. Note however that these figures show copper infiltration in two different locations on the brick. Refer again to figure 3. which illustrates those sample locations. Also use figure 3. to observe the location of sample #1, since figures 21.,22.,23., and 24. are taken from this sample. Figure 21. shows a composite x-ray map of the distribution of copper in this sample. Copper designated by the color blue appears as before to fill in areas of low relief. Figure 22. show the same area in black and white. Figure 23. is a combination of x-ray images and video image which allows easy tracing of the route taken by copper. Figure 24. an SEM micrograph shows the unique stretching effect of copper as it forms a connective network across sample #1-B. It was stated that copper was the only definate mineral found to have infiltrated the Sudbury brick. This is the only mineral that SEM analysis provided evidence for. However not detected in x-ray mapping is the presence of cuprite (Cu_2O), which was found in polished sections and x-ray diffraction patterns. The SEM elemental x-ray analysis program cannot detect oxides thus the reason cuprite was not found in any of the samples.

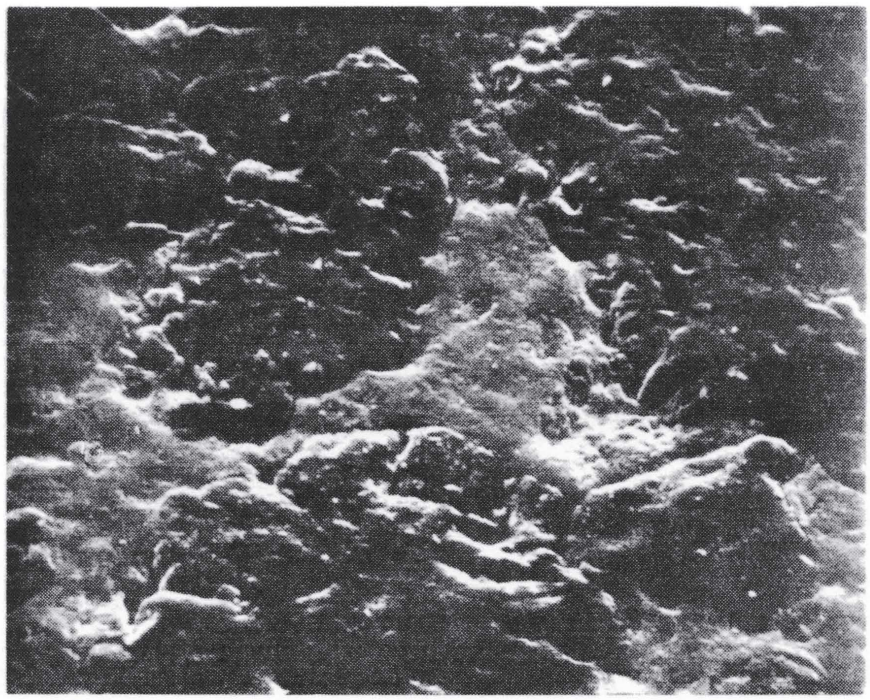

Figure 19.
SEM micrograph of sample #5-B showing infiltration of copper. Width of photo is 140 microns. Mag. 500x

Figure 20.
SEM micrograph of sample #7-A showing infiltration of copper. Width of photo is 50 microns. Mag. 2,200x

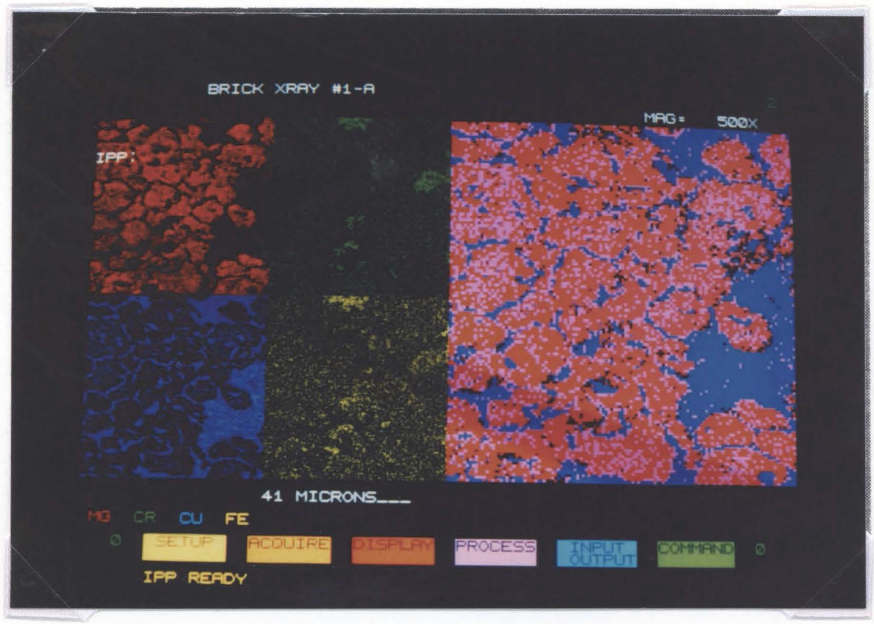

Figure 21.
Photograph of x-ray images and composite x-ray image showing distribution of Mg (red) and Cu (blue) in sample #1-A.

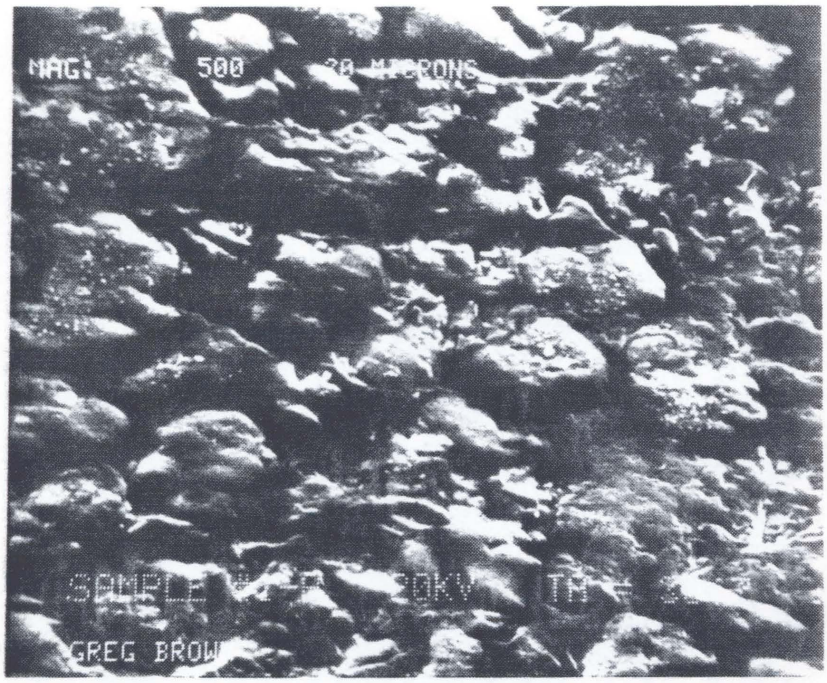

Figure 22.
SEM micrograph of sample #1-A. Use with above x-ray images to locate distribution of elements.

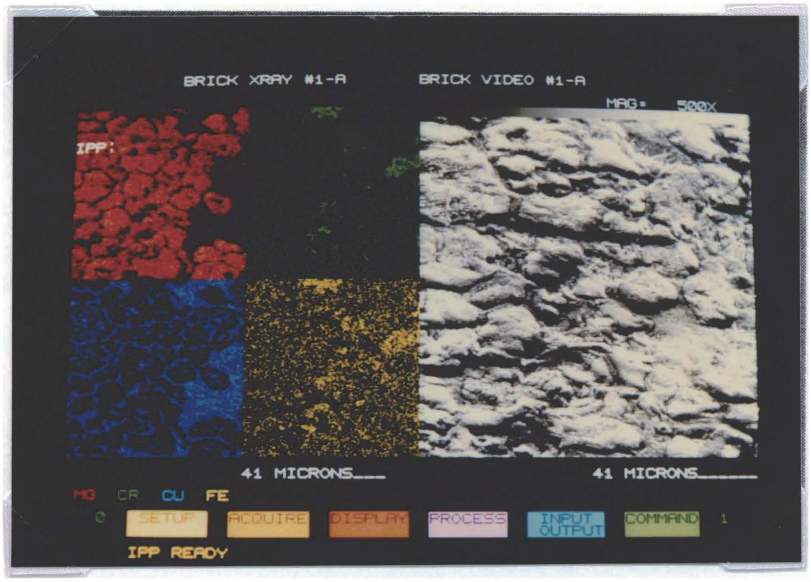

Figure 23.
Photograph of video and x-ray images of sample #1-A. Use with figures 21. & 22.

Figure 24.
SEM micrograph of sample #1-B showing infiltration of copper at high magnification.

X-RAY DIFFRACTION PATTERNS

To detect the presence of oxides as well as any other possible minerals, x-ray diffraction patterns were taken and polished and thin sections are described. The samples for x-ray diffraction are shown in figure 3., labeled A,B, C, and D at the bottom of the slab. X-ray patterns were acquired on samples A, B, and C which would provide an acceptable analysis of the brick. Preparation of these samples are described in appendix II. The three patterns recorded peaks from $2\theta = 6^\circ$ to $2\theta = 86^\circ$, this allowed many peaks to be gathered.

Sample A x-ray diffraction pattern showed a high concentration of copper and cuprite, with periclase peaks also strong. Also observed were chrome spinel peaks but to a lesser degree. This is consistant with the mineralogical analysis found found in a paper by A.V.Petty and E.Martin (1981), were they found chrome spinel, periclase, minor amounts of forsterite. Traces of cuprite were also found in their analysis. The x-ray diffraction patterns of the Sudbury brick showed higher concentrations of cuprite and only traces of forsterite as compared those found by Petty and Martin. Copper peaks were also found but to a lesser degree than that of cuprite.

Sample B x-ray pattern showed a very strong presence of chrome spinel with lesser amounts of periclase, copper and cuprite. Again only minor traces of fosterite was observed. Unlike sample A this sample showed a greater amount of copper than cuprite. This seems to be the trend as sampling went further into the brick.

Sample C showed large peaks of periclase and lower peak counts for chrome spinel and low peaks for copper and some for cuprite. However this sample also showed peaks for forsterite. This information indicated there is some forsterite but only in small amounts and more easily found near the center of the brick. Other evidence for the formation of cuprite is illustrated in polished sections.

POLISHED & THIN SECTIONS

Polished sections and thin-sections were prepared as descibed in appendix II. Thin sections although made with nearly all opaque material did comfirm the presence of one mineral. This meneral is micro-crystalline quartz and is scattered through-out the brick. This gangue mineral is one of the impurities mixed in when the brick was formed. It was observed that quartz was stained a yellowish color possibly from the oxidation of iron found through-out the brick. One interesting fact noted about the thinsections was that under crossed nicols the whole sample took on a red color. This overwhelming color is probably from the cuprite which has bright red internal reflections as illustrated in polished sections.

Polished sections showed a great deal more than the thin-sections as far as mineral identification. A prime example of this is shown in figure 25. and 26. Figure 25. shows the brilliant red internal reflections of cuprite under crossed nicols. Figure 26. shows the cuprite under uncrossed nicols. Notice the copper surrounding the cuprite. The scratches as well as the color in crossed and uncrossed nicols confirm this material as copper. Notice how the cuprite seems to form separate blebs. Many of these blebs become circular inclusions within the copper. Perhaps this disassociation effect between copper and cuprite is the reason that copper is only oxidized around the fringes of the brick, cuprite forms and separates, allowing copper to travel further into the brick.

Further evidence of copper migration is illustrated in figure 27. This figure shows copper (light colored) as flowing around crystals and filling in voids. The large crystal in the right portion of the figure is chrome spinel based on SEM analysis and petrographic properties. Another example of copper migration is shown in figure 28. The micrograph under uncrossed nicols clearly shows copper with spheroids of cuprite deposited between crystals. The cuprite

appears to have flowed in a north-east to south-west direction across the micrograph. Many of the cuprite spheroids are lined up behind one another possibly indicating faster flowing paths taken by copper.

Other interesting phenomena illustrated in polished sections are distinct color boundaries. These color boundaries are the same observed macroscopically in figure 1. Figure 29. illustrates one of these boundaries between a copper bleb located in the cement matrix and cement itself. The cement a darker contrast fills the bottom portion of the micrograph. The copper bleb with spheroids of cuprite forms the upper portion of the micrograph. This distinct boundary is present because the cement contains much more oxidized copper than the copper bleb. A similiar example is illustrated in figure 30. This figure demonstrates a boundary observed between the cement (top) and brick (bottom). Again notice the difference in amount of copper oxidation between the two materials.

To observe a boundary present in the brick itself figures 31. and 32. are included. In figure 31 cuprite infiltration is apparently stopped by the microcrystalline quartz. This is one such boundary that is visible macroscopically in figure 1. Cuprite had infiltrated past the oval grain (chrome spinel) and stopped at the edge of the quartz grain. This is some what visible in figure 32. which shows the same area under uncrossed nicols. The light colored grain in figure 32. is chrome spinel based on petrological analysis. The microcrystalline quartz grain appears wormy this is possibly due to thickness of the quartz grain. It appears periclase crystals have altered the appearence of this grain under uncrossed nicols. However it is evident there is a boundary illustrated in figures 31. and 32. and the reason for this is explained in the conclusion.

Figure 25.
Photomicrograph of cuprite in a copper bleb under crossed nicols. Photo witdth is 550 microns.
Mag. 200x

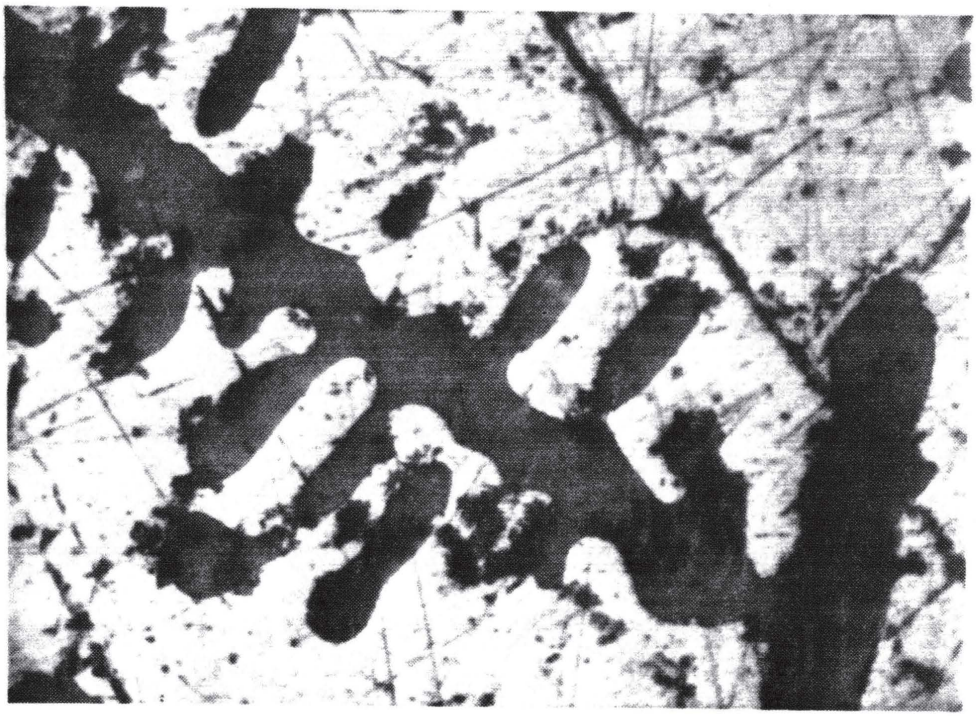

Figure 26.
Photomicrograph of curite under uncrossed nicols.
Photo width is 550 microns. Mag. 220x.

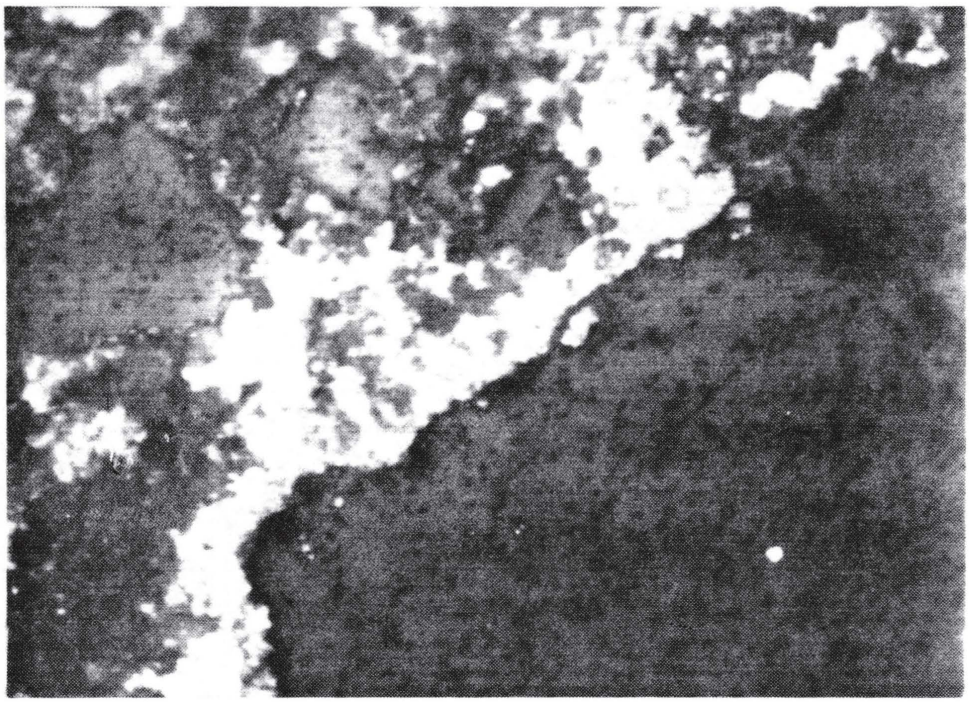

Figure 27.
Photomicrograph of copper infiltration around and between crystals under crossed nicols. Photo width is 1100 microns. Mag. 100x.

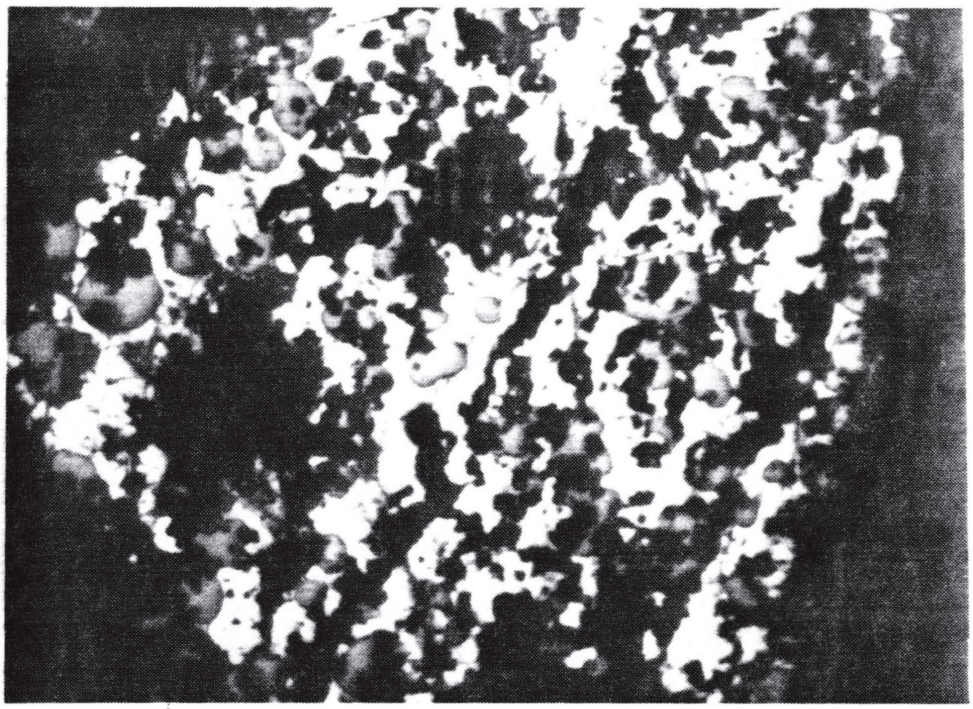

Figure 28.
Photomicrograph of copper and cuprite infiltration between crystals under uncrossed nicols. Photo width is 1100 microns. Mag. 100x.

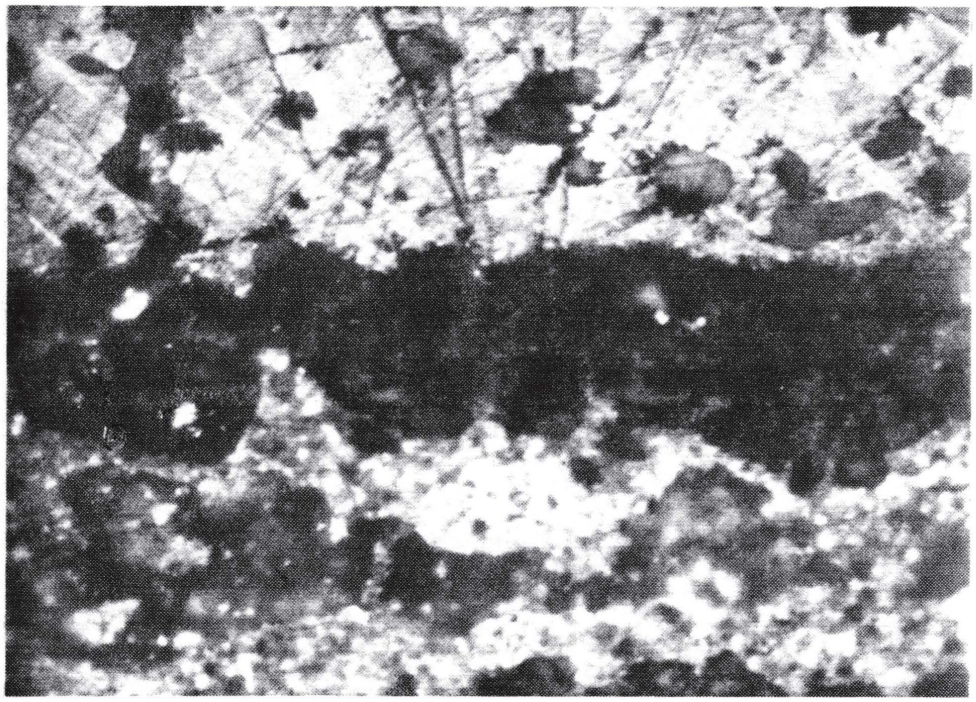

Figure 29.
Photomicrograph of copper bleb - cement boundary, under crossed nicols. Photo width is 1100 microns. Mag. 100x.

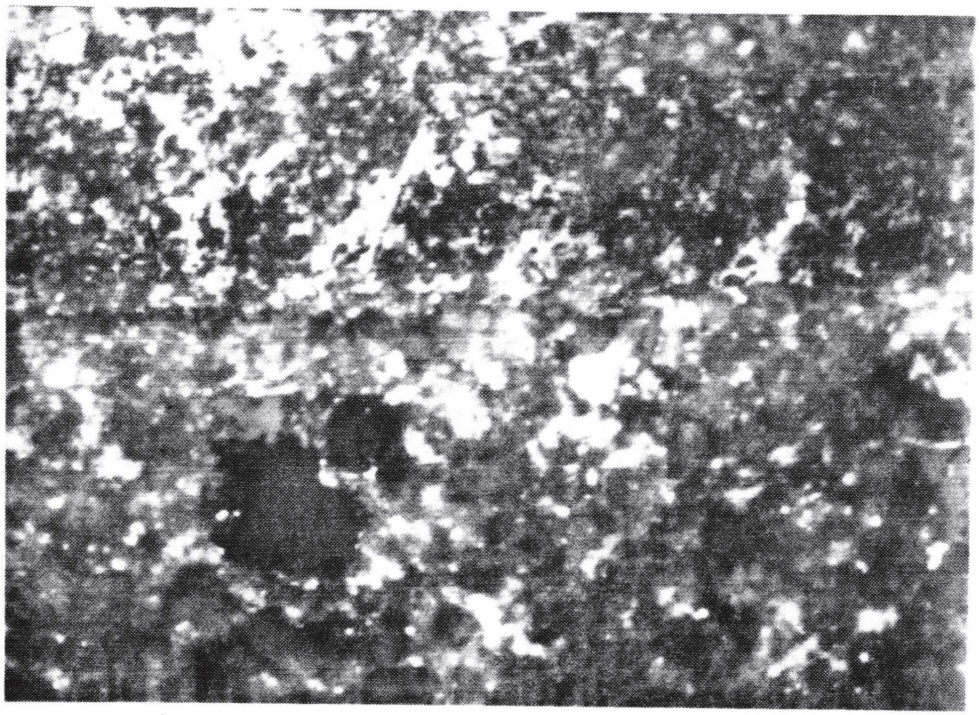

Figure 30.
Photomicrograph of cement - refractory boundary under crossed nicols. Photo width is 1100 microns. Mag. 100x.

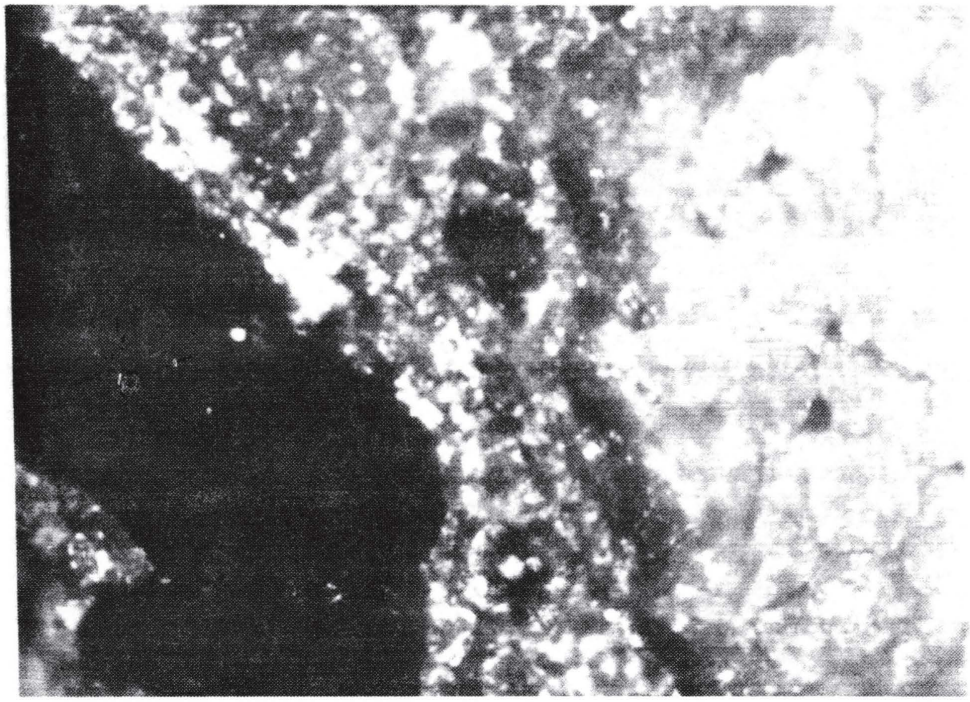

Figure 31.
Photomicrograph of infiltration boundary present in refractory under crossed nicols. Photo width is 1100 microns. Mag. 100x.

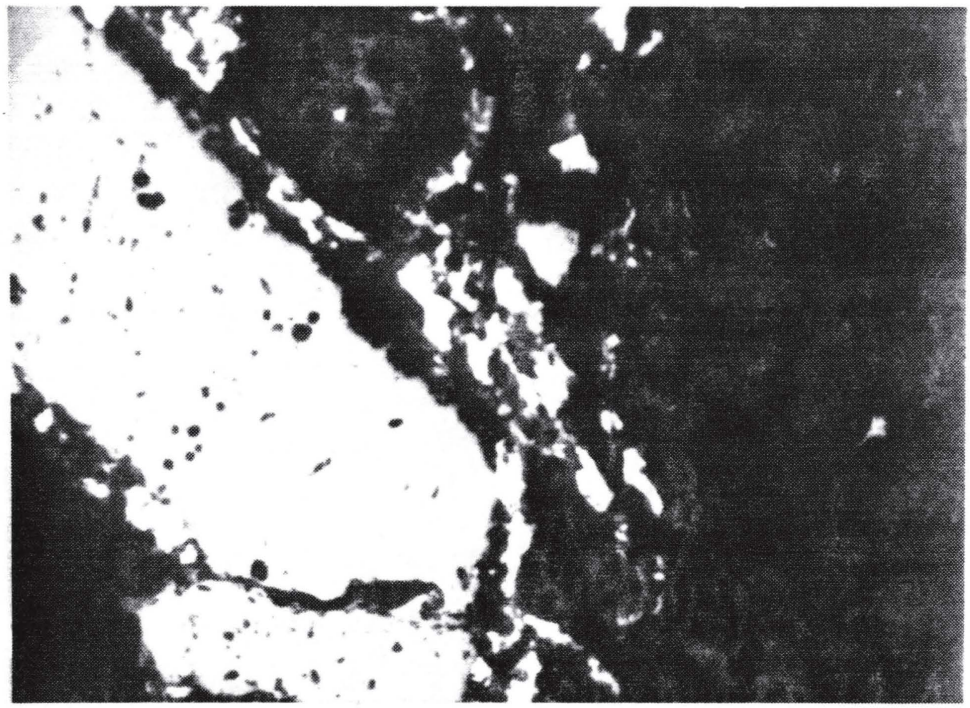

Figure 32.
Photomicrograph of infiltration boundary present in refractory under uncrossed nicols. Photo width is 1100 microns. Mag. 100x.

CONCLUSION

The title of this thesis explains the purpose of this report, that is to identify and interpret mineralogical infiltration in a chrome refractory collected in the Sudbury, Ontario Region. By briefly outlining the geology and history of this region insight was gained as to what minerals were to be searched for. A variety of techniques achieved this prupose since one would not provide sufficient data. SEM analysis provided the infromation of brick composition. As it is illustrated by numerous photos and micrographs. It appears the original composition of the brick before infiltration is periclase, chrome spinel and some forsterite. It was also demenstrated how minerals infiltrated this brick. This is explained by SEM micrographs showing large voids between crystals. The SEM mapping program not only explains what the crystals are but what infiltrated between them. X-ray composite images clearly show paths and networks formed by copper infiltration. But copper isn't the only mineral to infiltrate. It was x-ray diffraction patterns and polished sections which provided information on the infiltration of cuprite. It is these two minerals (copper and cuprite) which have infiltrated the Sudbury brick. The color changes observed in the first figure are the result of infiltration by copper and cuprite. It is the amount and quantity of each mineral that gives the color change its appearence. As illustrated in polished sections, boundaries between the color changes are the result of varying amounts of copper and cuprite. It was also explained that copper was found further in the brick than cuprite and it is this reason that color changes are observable. X-ray spectra did find traces of other elements possibly indicating other minerals have infiltrated. But these minerals would not be in sufficient quantities to effect a color change. A reason to explain the different rates of infiltration between copper and cuprite is that cuprite tends to disassociate from copper thus allowing for different flow rates.

Although cuprite is found in lower and lower amounts into the brick it is found as far or nearly as far in as copper. A possible explaination for such infiltration to the center of the brick is repeated furnace campaignes. Surges of new material enter the refractory at the start of every campaign. This could take on the appearence of advancing fronts. However the color of each front would still depend on the amount copper and cuprite present. Thus in conclusion the mineralogical infiltration is the result of varying amounts of copper and cuprite forming an observable color change (or front) in the Sudbury refractory.

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APPENDIXES

APPENDIX I

QUALITATIVE ELEMENT IDENTIFICATION

SAMPLE ID:BRICK SAMPLE #1

POSSIBLE IDENTIFICATION

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MG	KA					
CU	KA	KB			LA	
FE	KA	KB				
AL	KA					
SI	KA					
CA	KA					
S	KA					

PEAK LISTING

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2	1.252	7824	MG KA
3	1.504	3522	AL KA
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5	2.311	184	S KA
6	3.696	1251	CA KA
7	5.415	15138	CR KA
8	5.949	2045	CR KB
9	6.403	5381	FE KA
10	7.060	658	FE KB
11	8.037	6180	CU KA
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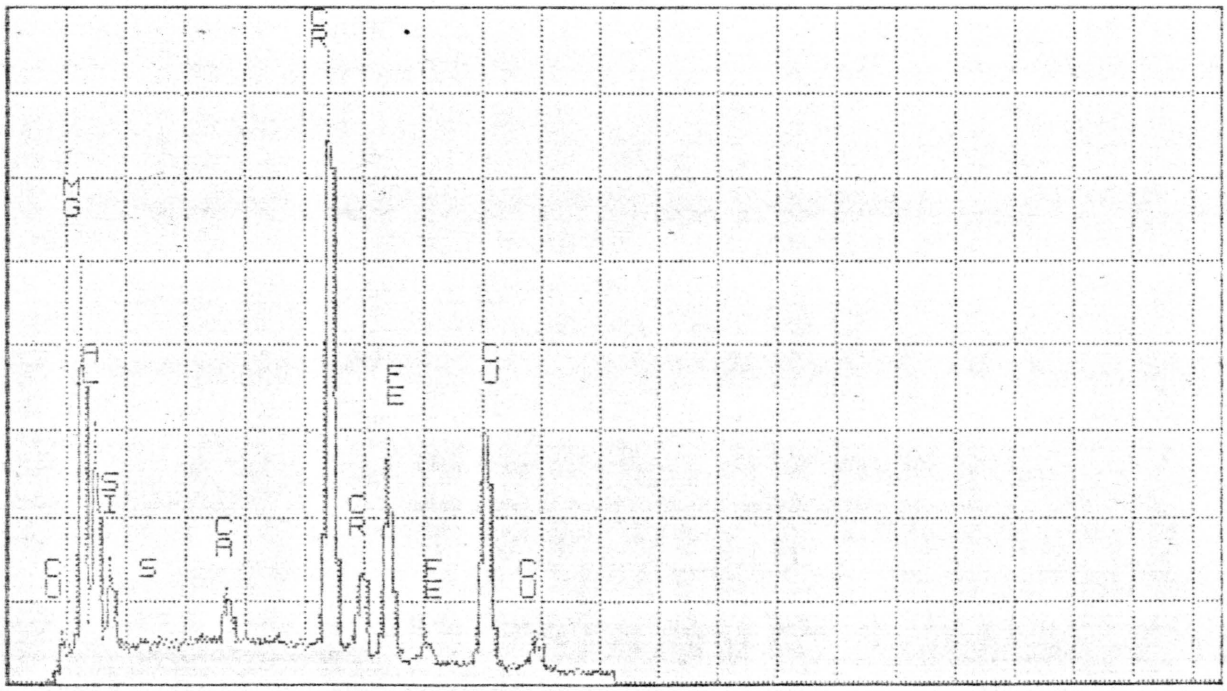

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SI KA
FE KA KB
CR KA KB OR PM LA LB
CA KA
AL KA
S KA
SC KA OR XE LA

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6	3.695	524	CA KA
7	4.091	193	SC KA
8	5.421	1562	CR KA
9	5.949	342	CR KB
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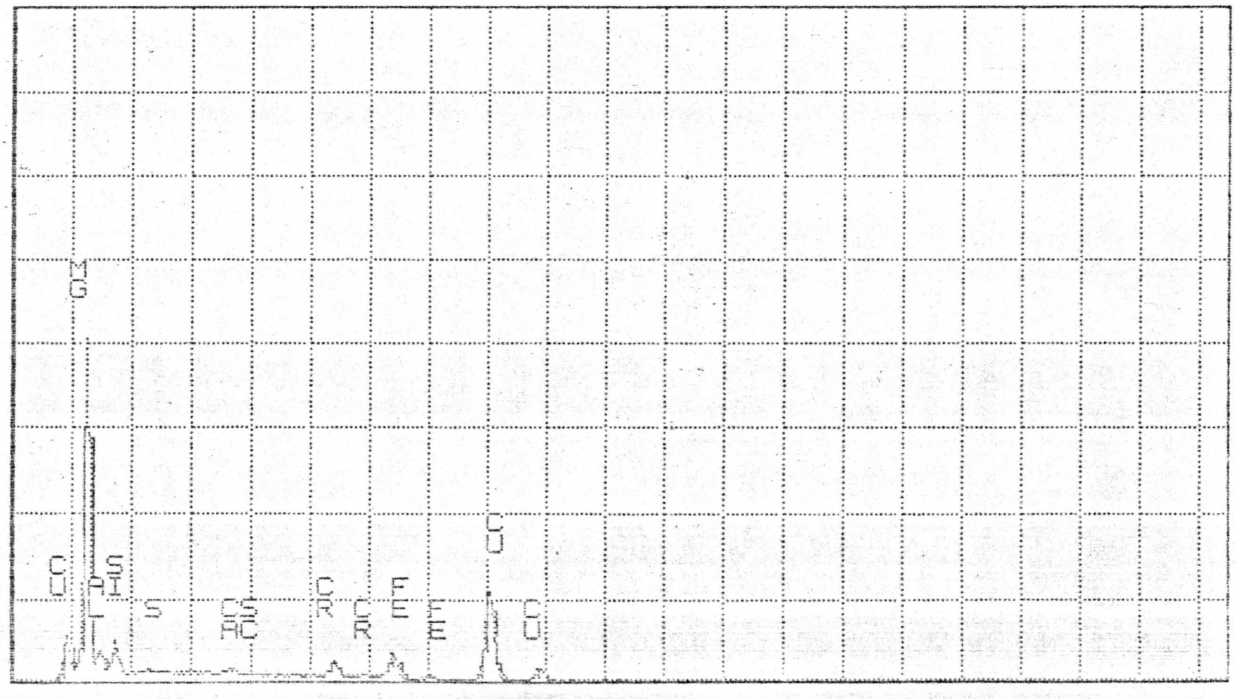

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SA BRICK SAMPLE #1-A

APPENDIX I

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SI KA
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K KA

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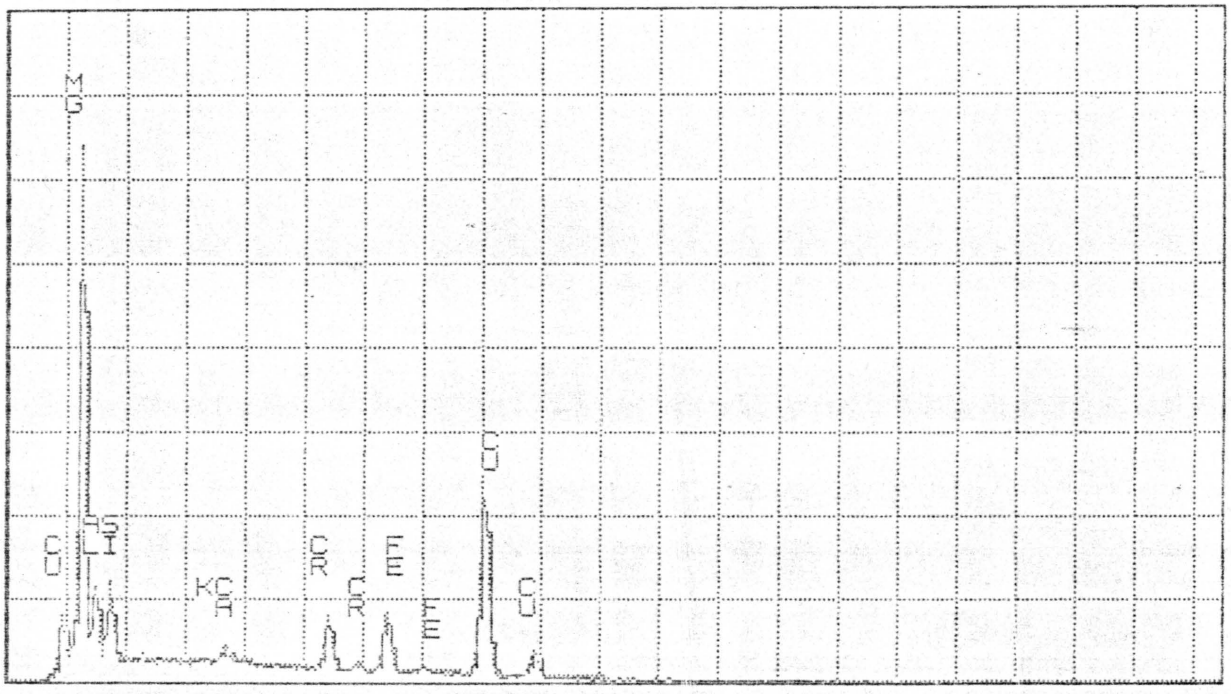

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   AL KA
   S  KA
   CA KA
   SI KA
   K  KA OR  IN LA?

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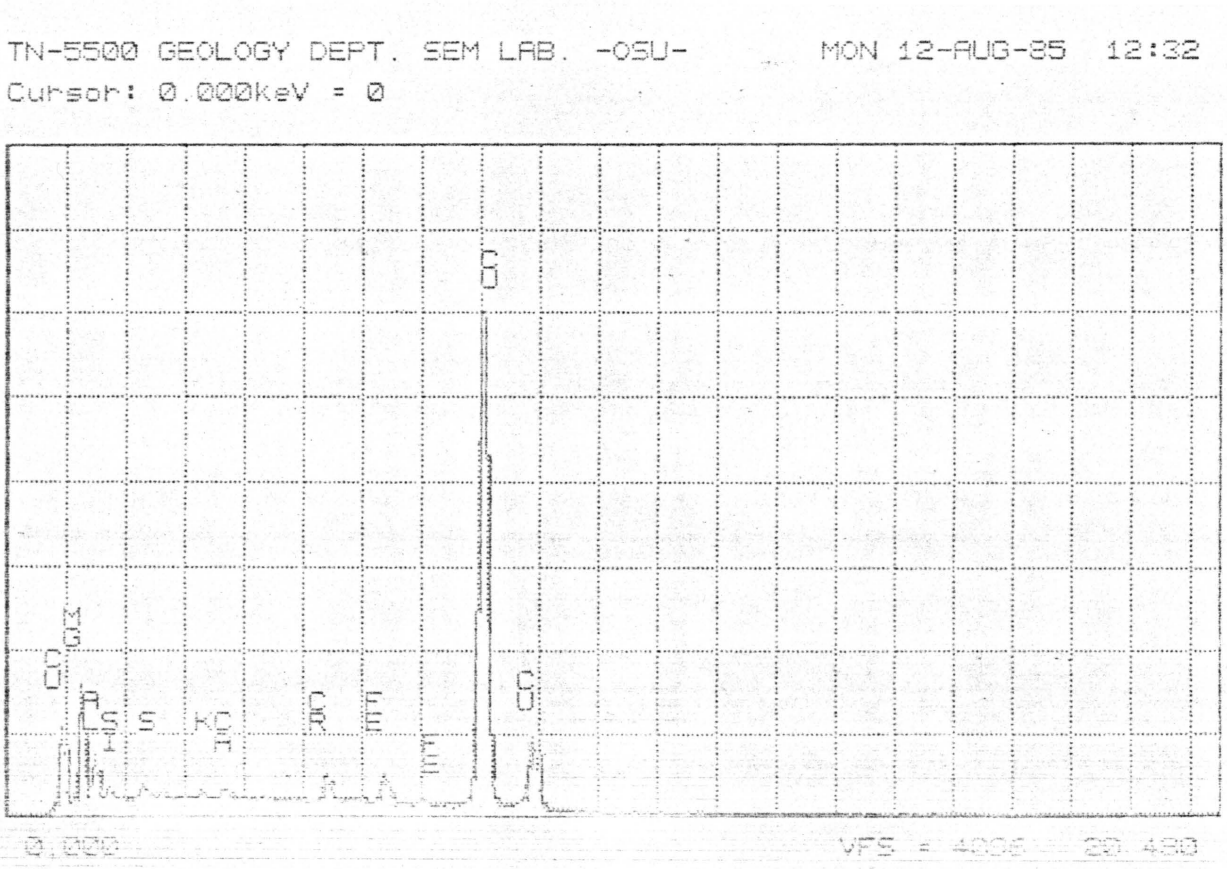

ID 4

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NI KA

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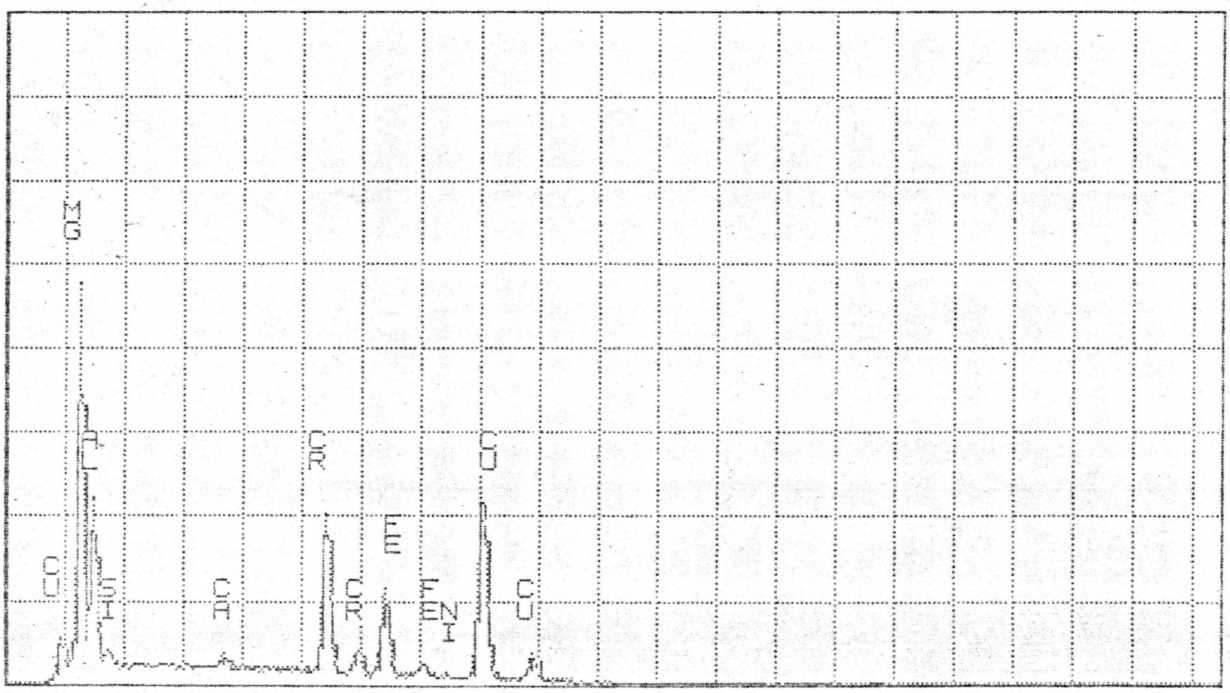

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AL KA
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CU KA
S KA
K KA OR IN LA?

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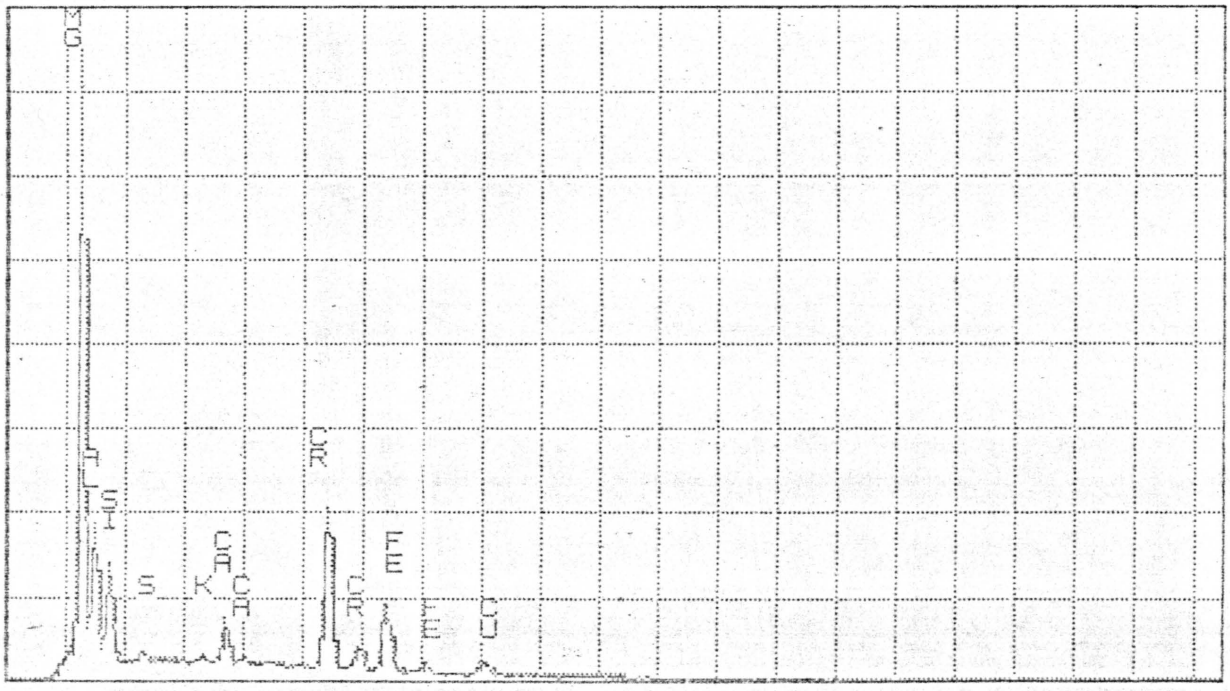

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50 BRICK SAMPLE #3-A

ID 4

QUALITATIVE ELEMENT IDENTIFICATION

SAMPLE ID:BRICK SAMPLE #3-B

POSSIBLE IDENTIFICATION
MG KA
CR KA KB OR PM LA LB
AL KA
FE KA KB
CA KA KB
SI KA
CU KA KB LA
S KA
K KA

PEAK LISTING

	ENERGY	AREA	EL. AND LINE
1	0.934	104	CU LA
2	1.254	14646	MG KA
3	1.507	4262	AL KA
4	1.761	1527	SI KA
5	2.310	524	S KA
6	3.319	295	K KA
7	3.699	1550	CA KA
8	4.028	202	CA KB
9	5.419	11234	CR KA
10	5.953	1440	CR KB
11	6.412	3473	FE KA
12	7.067	491	FE KB
13	8.048	854	CU KA
14	8.902	156	CU KB

IDENT:

TN-5500 GEOLOGY DEPT. SEM LAB. -OSU- WED 07-AUG-85 12:27
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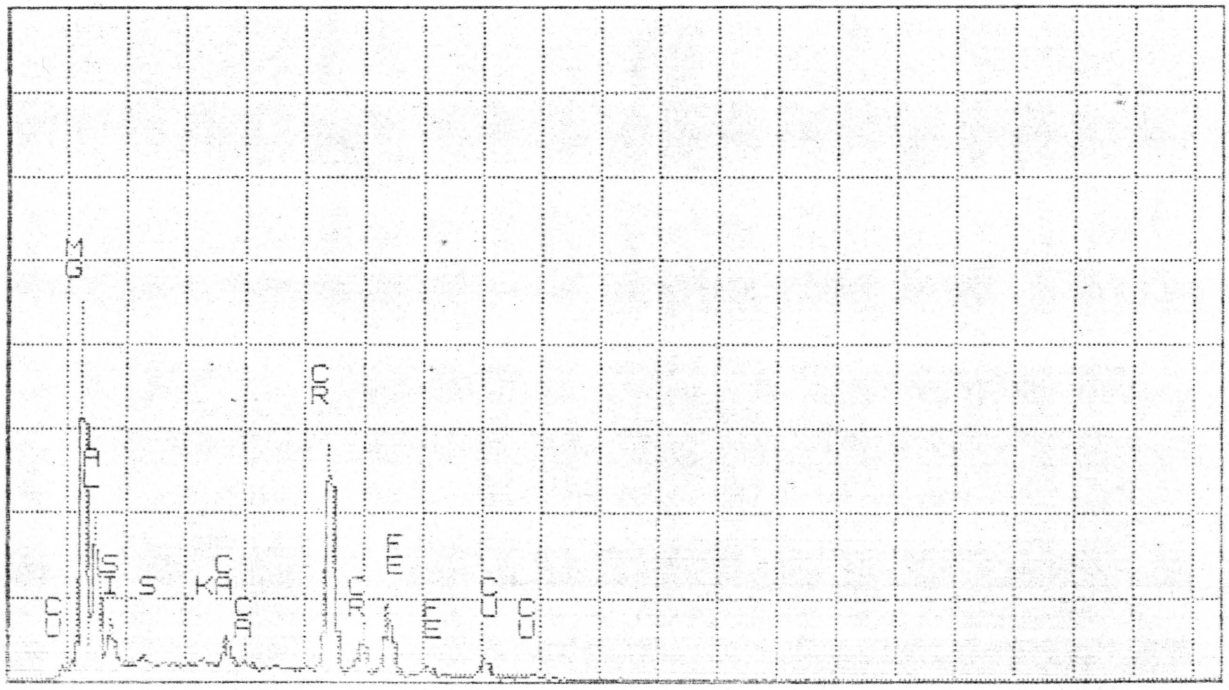

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10 BRICK SAMPLE #3-B

QUALITATIVE ELEMENT IDENTIFICATION

SAMPLE ID:BRICK SAMPLE #5-A

POSSIBLE IDENTIFICATION
MG KA
CR KA KB OR PM LA LB
FE KA KB
SI KA
CA KA KB
AL KA
CU KA KB LA
S KA OR TL LA MA
K KA
TL LA MA?

PEAK LISTING

	ENERGY	AREA	EL. AND LINE
1	0.942	98	CU LA
2	1.256	24932	MG KA
3	1.509	1955	AL KA
4	1.755	3197	SI KA
5	2.310	605	S KA OR TL MA?
6	3.331	413	K KA
7	3.699	2308	CA KA
8	4.034	177	CA KB
9	5.421	6667	CR KA
10	5.951	990	CR KB
11	6.410	3751	FE KA
12	7.053	560	FE KB
13	8.047	1424	CU KA
14	8.917	207	CU KB
15	10.240	102	TL LA

SSQ:

TN-5500 GEOLOGY DEPT. SEM LAB. -OSU- MON 12-AUG-85 13:11
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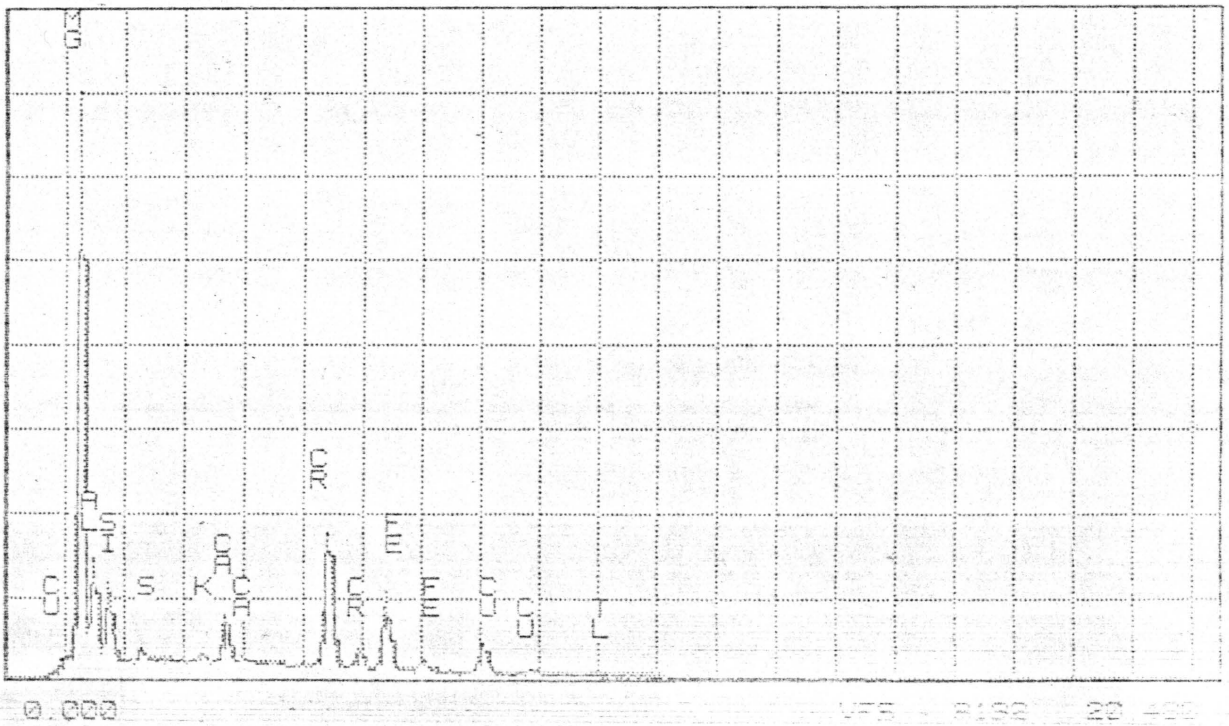

ID 4

QUALITATIVE ELEMENT IDENTIFICATION

SAMPLE ID:BRICK SAMPLE #5-B

POSSIBLE IDENTIFICATION
- 3 KA
- CU KA KB LA
- CR KA KB OR PM LA LB
- FE KA KB
- AL KA
- SI KA
- CA KA KB

PEAK LISTING

	ENERGY	AREA	EL. AND LINE
1	0.932	3695	CU LA
2	1.254	15869	MG KA
3	1.510	2282	AL KA
4	1.755	1932	SI KA
5	3.693	1659	CA KA
6	4.031	218	CA KB
7	5.416	4194	CR KA
8	5.937	599	CR KB
9	6.398	3605	FE KA
10	7.081	459	FE KB
11	8.037	11098	CU KA
12	8.898	1485	CU KB

IDENT:

TN-5500 GEOLOGY DEPT. SEM LAB. -OSU- THU 08-AUG-85 14:47

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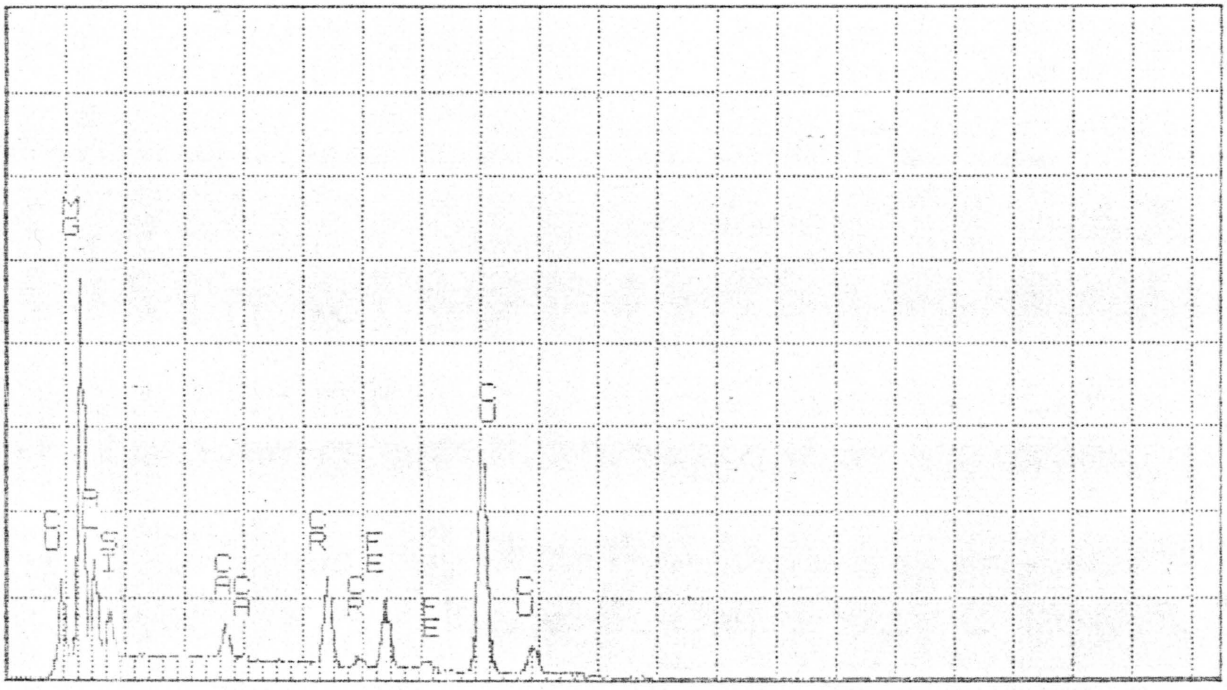

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50 BRICK SAMPLE #5-B

IDENT: ID 4

QUALITATIVE ELEMENT IDENTIFICATION

SAMPLE ID:BRICK SAMPLE #7-A

POSSIBLE IDENTIFICATION
R KA KB OR PM LA LB
AL KA
MG KA
CU KA KB LA
FE KA KB
CA KA
SI KA

PEAK LISTING

	ENERGY	AREA	EL. AND LINE
1	0.930	1986	CU LA
2	1.250	8929	MG KA
3	1.501	9054	AL KA
4	1.772	953	SI KA
5	3.706	1461	CA KA
6	5.421	12568	CR KA
7	5.951	1667	CR KB
8	6.408	4299	FE KA
9	7.053	509	FE KB
10	8.043	6525	CU KA
11	8.903	846	CU KB
12	10.171	184	UNIDENTIFIED

IDENT:

TN-5500 GEOLOGY DEPT. SEM LAB. -OSU- FRI 16-AUG-85 11:32
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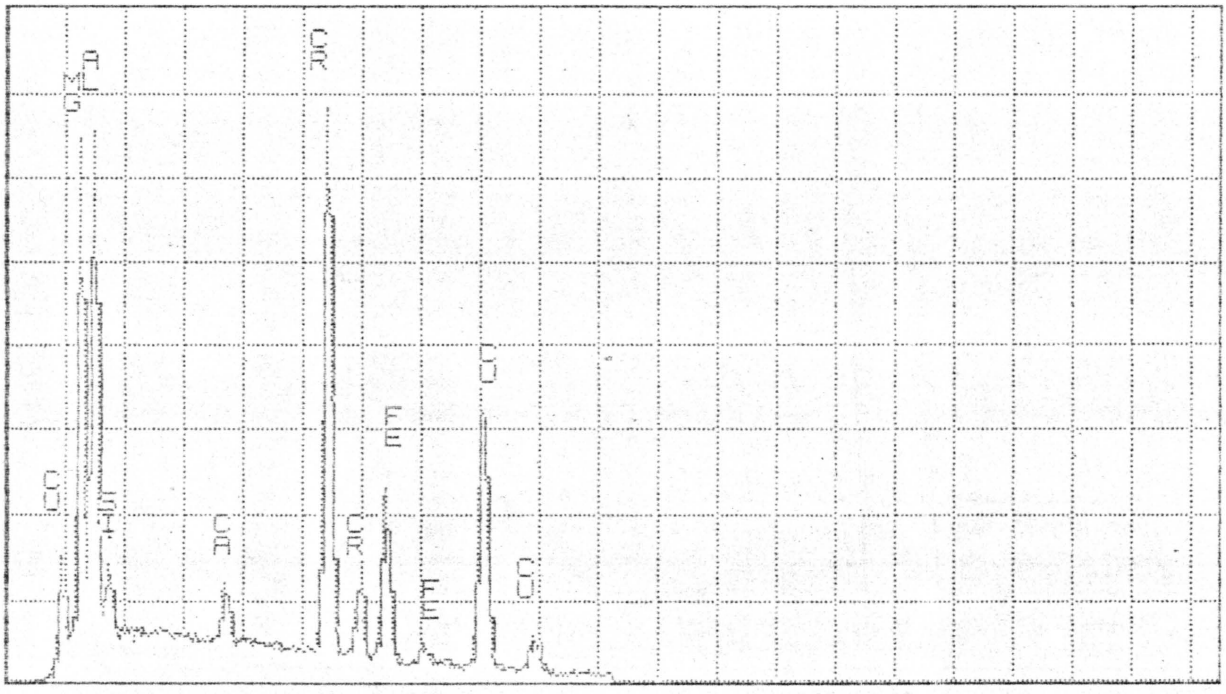

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50 BRICK SAMPLE #7-A

IDENT: ID 4

QUALITATIVE ELEMENT IDENTIFICATION

SAMPLE ID:BRICK SAMPLE #7-B

POSSIBLE IDENTIFICATION
MG KA
CU KA KB LA
CR KA KB OR PM LA LB
FE KA KB
SI KA
CA KA KB
AL KA
V KA KB?

PEAK LISTING

	ENERGY	AREA	EL. AND LINE
1	0.932	1790	CU LA
2	1.255	22360	MG KA
3	1.511	1718	AL KA
4	1.754	2853	SI KA
5	3.695	2108	CA KA
6	4.029	294	CA KB
7	4.969	251	V KA
8	5.416	3751	CR KA OR V KE
9	5.939	535	CR KB
10	6.399	3622	FE KA
11	7.041	525	FE KB
12	8.037	8072	CU KA
13	8.898	996	CU KB

IDENT:

TN-5500 GEOLOGY DEPT. SEM LAB. -OSU- THU 08-AUG-85 14:41
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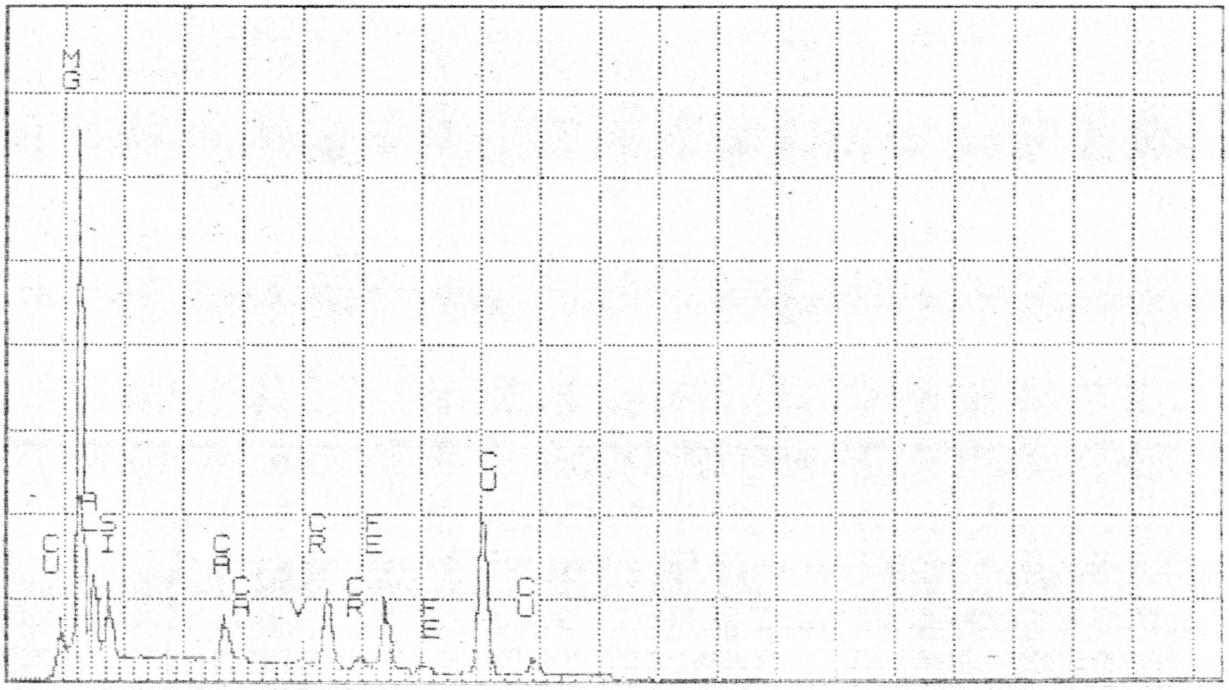

0.000 FS = 4096 20.480
50 BRICK SAMPLE #7-B

APPENDIX II

SEM SAMPLE PREPARATION

Sample preparation for the scanning electron microscope involved some work. In order to achieve good mapping data the speciems had to be polished for a relatively low surface relief. Second they had to be quite small; less than $\frac{1}{2}$ inch in diameter and only a few millimeters in thickness. To achieve the desired thickness a thin slab approximately 5mm thick was cut from the lenght of the brick. This slab was then polished down to 1,000 mesh grit. It was then sunk into plaster for support. A $\frac{1}{2}$ inch coring drill press was used to collect seven strategically placed samples. These samples were then cut down further in order to fit into the SEM. Figure 3. shows the specimen slab with specimens 1 thru 7 labeled, note specimen 4 and 6 were not used for SEM analysis. The remaining five specimens allowed for good representation of the color changes or infiltrated portion of the brick. The specimens were then coated with carbon in order to obtain mapping data.

Usually specimens coated with carbon instead of gold produce pitures of poor quality. However these specimens produced photos of good resolution and very good depth of field. Mapping data also turned out very good and was very useful in identify minerals. Specimens prepared this way also produced excellent SEM x-ray spectral data. Many elements were identified by their distinguishing peaks illustrated by the spectra.

APPENDIX II

X-RAY DIFFRACTION SAMPLE PREPARATION

To gather x-ray diffraction patterns samples were prepared from the lower portion of the slab in figure 3. Here four slide size specimens labeled A, B, C, and D were prepared for use in the x-ray diffraction machine. All were of the approximate size insertion into the machine except for thickness. They were polished down from 5mm to approximately 3mm in thickness so as to fit in the machine. Data was collected on samples A, B, and C which provided information on the mineralogy of the refractory.

APPENDIX II

THIN & POLISHED SECTION PREPARATION

Thin-sections were prepared by normal thin-sectioning techniques. Figure 1. illustrates a slab of brick from which the thinsections were taken. Note the distinct discoloration observed across the brick. It was my intention to make thinsections so that they would show this color change. It was decided that three thinsections would include not only the two distinct boundaries (fronts) between the three color changes but also the boundary between the brick and remnant cement. These three thinsections would provide a good representation of the brick yet it was realized that much of the material was opaque and useless in thinsection.

Knowing that the thinsections would contribute only a small amount of information, it was decided to make three matching polished sections in order to give a complete petrographic study of the brick. One way to achieve three identical polished sections that contribute the same information on the color changes, is to save the chips produced from the thinsectioning process. After the top portion of the brick slab was cut to produce three cubes, they were fastened to the glass slides. Completing the first cut of material from the glass slides, these chips were smoothed and labeled. The thin sections were finished and the matching chips were submitted for polish sectioning. Using both thin and polished sections the petrology of the opaque as well as the non-opaque minerals would be studied.